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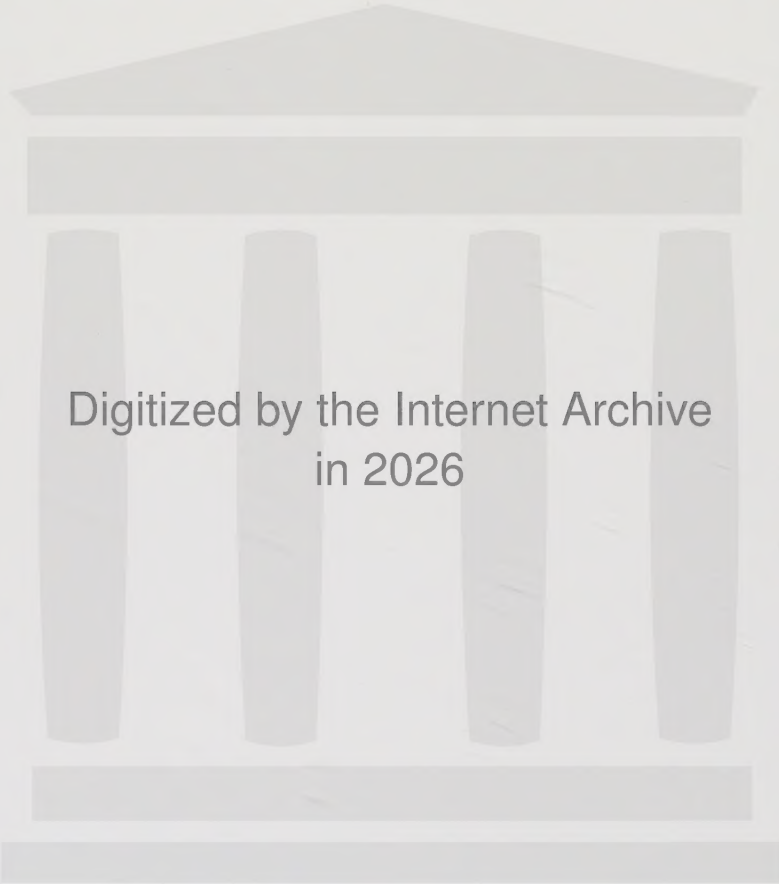


Rajinder K. Saxena

Oxygen-18 fractionation in nature and estimation of groundwater recharge

Uppsala University
Department of Physical Geography
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Report Series A
No 40



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To
Poonam and Priyank

ABSTRACT

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Some aspects of ^{18}O fractionation in the water cycle are studied in theory and practice with an aim to solve a few hydrological problems. From pan evaporation experiments it is inferred that for humid climates it is possible to predict with fair accuracy the fractionation occurring in a water mass and the δ value of the evaporate, which can be used to study the water balance of lakes. The weighted monthly mean $\delta^{18}\text{O}$ of precipitation is well correlated with monthly mean surface air temperature, the lapse rate varying from 0.25 to 0.48‰/°C, at Uppsala. It is observed that precipitation and vapour are in near isotopic equilibrium with each other during summer but not in winter. The interception loss in a pine forest at Uppsala was $\approx$ 40% of rainfall. The weighted mean $\delta^{18}\text{O}$ of throughfall was found to be enriched relative to rain by about 0.3‰. Simulated δ values of throughfall agreed closely with the observations. The ^{18}O depleted or enriched water (contributed by snowmelt or summer rains) that infiltrates in the soil has been used as an environmental tracer of soil moisture. From the vertical displacements of the "tagged" moisture layers, rates of soil moisture movement and percolation have been estimated. Annual recharge has been determined whenever soil moisture contributed by snowmelt of two consecutive years could be identified. In the sandy deposits in Uppsala the annual recharge varies from 200 to 300 mm. From the seasonal ^{18}O fluctuations in groundwater at Finnsjön, it was possible to identify local recharge-discharge zones.

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CONTENTS

1	PREFACE	11
2	INTRODUCTION	13
3	THE ISOTOPIC FRACTIONATION OF WATER	16
3.1	Some aspects of isotopic fractionation in liquid-gaseous phases in thermodynamical equilibrium.....	16
3.2	Fractionation during evaporation (equilibrium condition): The Rayleigh distillation formula	19
3.3	Fractionation in an open water body evaporating in an atmosphere under constant relative humidity and temperature.....	21
3.4	Fractionation in an open water body evaporating freely with an inflow (constant volume condition) in an atmosphere	28
3.5	Fractionation in an open water body from the mass and isotopic balance	30
4	PAN EVAPORATION EXPERIMENTS TO STUDY THE WATER BALANCE OF OPEN WATER BODIES	33
4.1	Introduction	33
4.2	Pan evaporation experiments at Uppsala	34
4.3	Experimental set-up	36
4.3.1	Monitoring of ^{18}O in atmospheric vapour	37
4.4	Results and discussions	39
4.5	Conclusions	46
5	SOME ASPECTS OF OXYGEN-18 IN PRECIPITATION	48
5.1	Seasonal effect	48
5.2	Continental effect	48
5.3	Latitude effect	48
5.4	Altitude effect	49
5.5	Amount effect	49
5.6	Temperature effect	50
5.7	Transport processes of atmospheric moisture and temperature effect in precipitation	51
5.8	Horizontal (advective) transport of atmospheric moisture and the temperature effect in precipitation	52
5.9	Eddy transport of atmospheric moisture and the temperature effect in precipitation	54
5.10	Temperature effect in precipitation at Uppsala	54
5.11	Oxygen-18 in atmospheric vapour in relation to specific vapour density	58
5.12	Oxygen-18 relationship between precipitation and atmospheric vapour	61
5.13	Oxygen-18 of atmospheric vapour at Uppsala	63
5.14	$\delta^{18}\text{O}$ vapour and temperature relationships at Uppsala	66

6	SAMPLING ERRORS IN OXYGEN-18 DUE TO FRACTIONATION IN RAIN GAUGES ...	68
6.1	Introduction	68
6.2	Experimental set-up	69
6.3	Results and discussions	69
6.4	Conclusions	71
7	OXYGEN-18 FRACTIONATION IN INTERCEPTION AND THROUGHFALL	73
7.1	Introduction	73
7.2	Isotopic fractionation in throughfall - some theoretical aspects	74
7.3	Field studies of interception and ^{18}O fractionation in throughfall	77
7.4	Results and discussions	78
	7.4.1 Canopy reservoir capacity and rainfall-throughfall relationships	78
	7.4.2 Fractionation in throughfall	83
7.5	Conclusions	86
8	ESTIMATION OF GROUNDWATER RECHARGE AND SOIL MOISTURE MOVEMENT BY ISOTOPIC TRACERS.....	87
8.1	Introduction	87
8.2	Radiotracers in estimation of groundwater recharge - a brief review	88
8.3	Use of stable isotopes for estimation of groundwater recharge and rates of soil moisture movement	92
8.4	Moisture movement and recharge estimates - some theoretical considerations	93
8.5	Oxygen-18 as a tracer for recharge estimations: field studies	95
8.6	Description of sites	97
8.7	Experimental methodology	97
	8.7.1 Field sampling of soil moisture	98
	8.7.2 Laboratory extraction of moisture from soil cores or samples	100
8.8	Results and discussions	102
	8.8.1 Comparison of ^{18}O and ^3H methods	102
	8.8.2 Moisture movement and estimation of seasonal recharge by ^{18}O	105
8.9	Field variability of ^{18}O in soil moisture	118
8.10	Conclusions	120
9	FRACTIONATION IN THE UNSATURATED ZONE	121
9.1	Fractionation due to evapotranspiration from soils	121
9.2	Fractionation in lysimeter percolates in bare soil	124
9.3	Conclusions	126

10	SEASONAL FLUCTUATIONS OF OXYGEN-18 IN GROUNDWATER IN FISSURED ROCK	128
10.1	Introduction	128
10.2	Seasonal variations of ^{18}O in groundwater in fissured rock at Finnsjön	129
10.3	Site description	129
10.4	Experimental procedure	130
10.5	Comparison of sampling methods	130
10.6	Results and discussions	132
10.7	Conclusions	138
11	CONCLUDING REMARKS	139
	REFERENCES.....	142
	LIST OF SYMBOLS.....	150

1 PREFACE

During the past few decades, stable isotopes of oxygen (^{18}O) and hydrogen (D) have found increasing applications in the field of hydrology. Some of the studies were aimed at understanding the basic principles of isotopic fractionation during evaporation-condensation of water, while others used ^{18}O and D as natural tracers of water and its flow path, more or less on a qualitative basis.

The first part of this thesis deals with some theoretical aspects of ^{18}O fractionation in natural waters. In the later sections, the knowledge gained from theory and experiments is applied to solve some field problems in hydrology. The main thrust of this work is to estimate percolation and groundwater recharge using ^{18}O as an environmental tracer, together with surface and groundwater interactions. Such a study required a proper understanding of the isotopic composition of precipitation, atmospheric vapour, their interdependence and temperature relationships. As the study progressed, the need to study a few more aspects of ^{18}O fractionation in the water cycle became apparently clear, resulting in the estimation of sampling errors in ^{18}O in the rain gauges, enrichment or depletion of throughfall from the tree canopy and the canopy interception loss.

The study was financially supported by NFR, the Swedish Natural Sciences Research Council, in the form of a project. The project consisted of two subprojects. I was responsible for the subproject: Estimation of groundwater recharge by ^{18}O .

The project was initiated and supervised by Professor Erik Eriksson (now Professor Emeritus), ran smoothly during the short tenure of Professor Lars Gottschalk and culminated under the leadership and supervision of Professor Lars Bengtsson.

I wish to acknowledge my deep and heartfelt thanks to Professor Lars Bengtsson for his able supervision, clear guidance and keen interest in the project. He also read the manuscript very critically and gave many useful comments and suggestions. Without his moral and scientific support this work would not have easily seen the light of the day.

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Thanks are also due to Fil Kand Allan Rodhe (responsible for the subproject: Study of runoff processes by ^{18}O) for his active collaboration in the pan evaporation experiments, sampling errors in ^{18}O due to fractionation in rain gauges, some theoretical aspects of isotope balance (Section 3.5) and general help at various stages of this work.

The collaboration of Swedish Geological AB in giving the logistics support and Swedish Nuclear Fuel and Waste Management Company (SKB) in providing the equipment and expertise for pumping tests in Finnsjön is gratefully acknowledged. Thanks to Fil Kand Erik Gustafsson and Fil Kand Jan-Åke Jacobsson for their cooperation in Finnsjön, and to Dr J. O. Burgman and Civ Eng Frank Westman for keeping the mass-spectrometer at my disposal.

Thanks to Mr Sören Karlsson for his expertise in the construction and repair of most of the field equipment. Dr Bengt Calles drew most of the figures and Mr Assar Lindberg did the photographic work.

Thanks to Ms Kristina Nilsson who patiently typed the manuscript on the word processor and gave valuable help in editing also. Dr Rolf Larsson read the proofs.

Last but not least I wish to record my appreciation for the persevering patience and moral support of my wife Poonam during all these years.

Uppsala, March 1987

Rajinder K. Saxena.

2 INTRODUCTION

With the discovery of isotopes in the 20th century, intense research has been devoted to the stable isotopic components of water, namely ^{18}O as (H_2^{18}O) and D as (HD^{16}O). Physicists were mainly interested in determining their physical properties, i.e. boiling and freezing points, density, saturated vapour pressure, etc. Noteworthy is the slowing down power of HDO for fast neutrons, which eventually found use in the (heavy water moderated) nuclear reactors for commercial purposes. Hydrologists on the other hand exploited the less glamorous properties, most important of which is the vapour pressure. The saturated vapour pressure of H_2^{18}O is lower than H_2^{16}O , and so is the case for HDO relative to H_2O as well. With the improvements in mass-spectrometric techniques in the mid50s, it became easier to handle a large number of samples with high accuracy (0.1‰ and 1‰ for ^{18}O and D, respectively) and stable isotope hydrology became an established discipline of hydrology. Realizing the tremendous potential of stable isotopes in hydrology, the International Atomic Energy Agency (IAEA) in Vienna undertook a world-wide survey of ^{18}O and D in precipitation in joint collaboration with WMO. The collected data have been continuously published since 1960 as an inventory of environmental isotopes in precipitation. Since 1963, IAEA has conducted symposia on isotope hydrology, roughly every four years, in which contributions dealing with stable isotopes continue to increase.

The scientific interest in the isotopic composition of precipitation started rather early. Riesenfeld and Chang (1936a, b) reported that winter precipitation is isotopically lighter than summer precipitation. This observation was later confirmed by Dansgaard (1954) and other workers on a global scale. The early work of Epstein and Mayeda (1953) showed that well mixed ocean water has an almost constant composition of ^{18}O and D. It has been found that the mean ocean water has about 2000 ppm ^{18}O and about 320 ppm D. The abundance of ^{18}O obtained from different natural sources showed a variation of about 10%. Thus, it became meaningless to speak of the abundance of ^{18}O or D unless the source of the sample analysed was properly specified. At present, for the sake of convenience, the relative deviation in the isotope abundance ratio of a sample with respect to a reference is determined. If the absolute ratio of the heavy to

the most abundant isotope in a sample is R_{sample} and the corresponding ratio in the standard water is R_{STD} , then the relative deviation δ is expressed as

$$\delta_{\text{sample}} = \{(R_{\text{sample}} - R_{\text{STD}})/R_{\text{STD}}\} \quad (2.1)$$

The δ values are often expressed as per mille.

The reference standards could be any of the following, e.g. SMOW (Standard Mean Ocean Water), V-SMOW (Vienna SMOW), GISP (Greenland Ice Sheet Precipitation), NBS (National Bureau of Standards), SLAP (Standard Light Antarctic Precipitation) and PDB, PDPB, etc. In this work, all the results are given relative to Vienna SMOW.

The important features of stable isotope research in the realms of hydrology can be summarized in a nutshell such as

- a) Fresh waters are found to be depleted in heavy isotopes as compared to sea water, Epstein and Mayeda (1953).
- b) The oceans have a fairly constant isotopic composition excluding those pockets which have huge inflows of fresh waters, Epstein and Mayeda (1953).
- c) There is a parallel variation in ^{18}O and D contents in fresh waters, the relationship being $\delta\text{D} = 8\delta^{18}\text{O} + 10\text{‰}$, called the Craig's or meteoric line, Craig (1961).
- d) The heavy isotopic composition of precipitation can be expressed as a function of condensation temperature. ^{18}O and D contents in precipitation decrease with decrease in condensation temperature, Dansgaard (1954).
- e) The heavy isotopic content in precipitation decreases with increasing latitude (latitude effect), altitude (altitude effect), and there is a seasonal isotopic variation of precipitation not only at high latitudes but also in subtropical areas, Epstein and Sharp (1959) and Dansgaard (1961, 1964).
- f) The parallelism between ^{18}O and D (as in c) is disturbed during fast evaporation due to kinetic effects, Dansgaard (1964).
- g) The isotopic interaction or exchange between an evaporating water body and the atmosphere is considerable and cannot be neglected, Craig and Gordon (1965).
- h) Generally, groundwater in nongeothermal areas has almost the same isotopic content as precipitation, Gat (1971).

On the basis of the above findings, efforts have been made to study various aspects of the hydrological cycle. For example, studies on the origin of groundwater on a regional scale, surface and groundwater interactions, lake water balance, leakage from reservoirs, groundwater recharge, paleoclimates, glaciology and moisture circulation patterns etc., have been carried out in a variety of climatic conditions with varied degree of success.

Among the above, estimation of groundwater recharge is a challenging problem. It was only two decades ago that radiotracers were successfully employed to study the downward movement of soil moisture and groundwater recharge, circumventing the problem of determining the hydraulic conductivity and hydraulic gradients in the field. Though it was recognized that stable isotopes (^{18}O , D) may also be used as tracers for the above studies, yet no serious attempt has been made so far in this regard specially in humid climates.

The main advantage of stable isotopic tracers is that they need not be introduced or injected (in the system under investigation) and are a part of the environment, eliminating pollution problems. ^{18}O and D are gaining popularity as scepticism about radio-tracer introduction in the environment is increasing every day for the sake of preserving ecology.

The present work is an attempt to quantify the rate of soil moisture movement and recharge using the seasonal variations of ^{18}O in precipitation as a natural tracer of soil moisture. Such a study requires a detailed knowledge of the fundamentals of isotopic fractionation processes occurring in natural evaporation-condensation and exchange. The following aspects of ^{18}O fractionation in nature with some applications in hydrology are discussed in this presentation:

1. ^{18}O fractionation in evaporation-condensation of a water mass .
2. General views and case studies of ^{18}O in precipitation, atmospheric vapour, vapour transport processes and fractionation in throughfall from tree canopy.
3. Estimation of soil moisture movement, groundwater recharge and fractionation in bare soils.
4. Surface and groundwater interactions in fissured rocks.

The locale settings are mostly in and around Uppsala township, Sweden.

3 THE ISOTOPIC FRACTIONATION OF WATER

Apart from evaporation-condensation, the isotopic fractionation of water is also due to exchange processes (water-rock, water-gas) and some biological activities. Among these, fractionation due to exchange and evaporation-condensation are of consequence to hydrology and will be discussed here.

The fundamental reason for isotope fractionation in a water mass undergoing evaporation is the difference between saturation vapour pressure of heavy and light molecules of water. For example $P(H_2^{16}O)$ is higher than those of $P(H_2^{18}O)$ and $P(HD^{16}O)$; "P" stands for vapour pressure. The preferential removal of the light ($H_2^{16}O$) molecules from the liquid phase increases its heavy ($H_2^{18}O$) isotopic content. In other words, as evaporation proceeds, the liquid phase gets more and more enriched.

The evaporation process can be considered under equilibrium and non-equilibrium conditions. The equilibrium evaporation of water seldom occurs in nature but condensation from clouds is considered as a near-equilibrium process (Dansgaard, 1961). It is thus interesting to discuss evaporation-condensation when:

a) water and vapour are in equilibrium (ideal case)

and

b) natural evaporation of water taking place in non-equilibrium conditions.

3.1 Some aspects of isotopic fractionation in liquid-gaseous phases in thermodynamical equilibrium

Consider the thermodynamical equilibrium between water and vapour in a closed system. Initially the gaseous phase consisted of the heavier isotope, ^{18}O , and the liquid contained only the most abundant isotope ^{16}O . When both phases have attained thermodynamical equilibrium, then the exchange reaction can be written as



where O^* signifies ^{18}O and O is ^{16}O , subscripts l and g denote liquid and gaseous phases.

In terms of the concentrations and partial pressures, the equation for this reaction can be written as

$$[H_2O^*]PH_2O = K[H_2O]PH_2O^*$$

$$\text{or } \frac{[H_2O^*]}{[H_2O]} = K \frac{PH_2O^*}{PH_2O} \quad (3.1)$$

Equation (3.1) expresses the ratio of the concentration of the heavy component to light component in the liquid phase which is directly proportional to the ratio of the partial pressure of the heavy component to the light component in the gaseous phase and K is the equilibrium constant. For a system in equilibrium, where there is only one atom of the exchangeable isotope in each of the reacting molecules, the equilibrium constant K is synonymous with the unit separation factor or the fractionation factor α , i.e. $\alpha = K$; Urey (1947) and Ferronsky and Polyakov (1982). Urey (1947) has also shown for such type of reactions that the symmetry numbers of the two isotopic molecules are the same and their ratio = 1. In more complicated reactions, where several atoms of the exchangeable isotopes in each molecule are involved, then $\alpha \neq K$.

However, for the isotopic exchange of oxygen in the CO_2 -water system,



it can be shown that in this particular case also, $\alpha = K$.

A very elegant and complete discussion on the relationship between α and K is given by Ferronsky and Polyakov (1982).

Equation (3.1) represents the thermodynamical equilibrium between a liquid and a gaseous phase. If R_l is the ratio of the concentrations of the heavy to light component in the liquid phase and R_g the corresponding ratio in the gaseous phase, then eq.(3.1), in terms of fractionation factor α , is reduced to the form

$$R_l = \alpha R_g \quad \text{such that} \quad \alpha > 1 \quad (3.2)$$

The fractionation factor α has been found to be temperature dependent.

From the relative volatilities of the system $H_2^{16}O-H_2^{18}O$, Zhavoronkov et al. (1955) gave a general expression for obtaining $\alpha(^{18}O)$, between 20 to 90°C

$$\alpha(^{18}O) = \frac{1}{.9822 e^{(15.788/RT)}} \quad (3.3a)$$

Majoube (1971b) gave the following relationship for ^{18}O fractionation between water-vapour in the temperature range 0-100°C

$$\ln\alpha(^{18}O) = \left(\frac{1.137 \cdot 10^3}{T^2}\right) - \left(\frac{0.4156}{T}\right) - 2.0667 \cdot 10^{-3} \quad (3.3b)$$

while Bottinga (1975), as reported by McKenzie & Truesdell (1977), gave the following form in the temperature range 3-300°C

$$\ln\alpha(^{18}O) = \left(\frac{0.7664 \cdot 10^3}{T^2}\right) + \left(\frac{1.2051}{T}\right) - 0.003494 \quad (3.3c)$$

In the above equations R = gas constant and T is in °K.

It is however difficult to measure α values below the freezing point of water, but Dansgaard (1964), in order to study the condensation process in clouds, obtained $\alpha(^{18}O)$ values down to -20°C by extrapolating eq.(3.3a) of Zhavoronkov et al.

For ^{18}O fractionation between ice-vapour, Majoube (1971a) gave the relationship

$$\ln\alpha(^{18}O) = \left(\frac{11.839}{T}\right) - 28.224 \cdot 10^{-3} \quad (3.3d)$$

From eqs (3.3a to 3.3c), the $\alpha(^{18}O)$ at 0° and 20°C obtained by different workers are:

0°C	20°C	
1.0111	1.0091	Zhavoronkov et al. (1955)
1.0117	1.0098	Majoube (1971b)
and 1.0112	1.0096	Bottinga (McKenzie & Truesdell, 1977)

Values of $\alpha(D)$ have been measured by Merlivat et al. (1963) and according to them, $\alpha(D)$ at 1° and 20°C is 1.104 and 1.079 respectively.

The isotopic exchange between water and CO_2 is of special interest in mass-spectrometry, where the ^{18}O content of water is measured by equilibrating CO_2 with a water sample, and analysing CO^{18}O by the mass-spectrometer. Different workers have obtained $\alpha(^{18}\text{O})$ for isotopic exchange between the $\text{H}_2\text{O}-\text{CO}_2$ system at 25°C , which are

1.0407 ± 0.0003	Compston & Epstein (1958)
1.0407 ± 0.0004	O'Neil & Epstein (1966)
and 1.0409 ± 0.0002	Bottinga & Craig (1969).

It is clear that the values of $\alpha(^{18}\text{O})$ for water-vapour and the $\text{H}_2\text{O}-\text{CO}_2$ system obtained by different workers are essentially the same. However, for the water-vapour system the values given by Majoube (1971b) and Bottinga (1977) are generally preferred. For the $\text{H}_2\text{O}-\text{CO}_2$ system, the choice is simply a matter of taste.

3.2 Fractionation during evaporation (equilibrium condition): the Rayleigh distillation formula.

Consider a system where water is slowly evaporating, the vapour is assumed to be removed immediately from the system such that equilibrium exists or virtually exists at the water-vapour interface.

Let N_1^* and N_1 be the number of heavy (H_2^{18}O) and light (H_2^{16}O) molecules in the liquid phase, respectively. Similarly let N_g^* and N_g be the number of heavy and light molecules in the vapour phase. The ratio of heavy to light components in the liquid phase $R_1 = N_1^*/N_1$ and the corresponding ratio in the vapour phase $R_g = N_g^*/N_g$. Since the system is in equilibrium, $R_1 = \alpha R_g$ at every stage of evaporation, also ($\alpha > 1$). Here α is the unit separation factor or equilibrium fractionation factor.

The immediate removal of a small quantity dN_1 of H_2^{16}O molecules from the liquid phase corresponds to a removal of $d(R_1 N_1)$ molecules of H_2^{18}O . Since dN_1 is the removal of H_2^{16}O , the amount of H_2^{18}O removed from the vapour would be

$$R_g dN_1 = \frac{R_1}{\alpha} dN_1$$

$$\text{or } d(R_1 N_1) = R_g dN_1 = \frac{R_1}{\alpha} dN_1$$

$$\text{or } \frac{dR_1}{R_1} = \frac{dN_1}{N_1} \left(\frac{1}{\alpha} - 1 \right)$$

Integrating this expression between the limits R_0 to R_1 and N_0 to N_1 , we get

$$\ln \frac{R_1}{R_0} = \ln \frac{N_1}{N_0} \left(\frac{1}{\alpha} - 1 \right)$$

$$\text{or } R_1 = R_0 f^{(1/\alpha - 1)} \quad (3.4)$$

where $f = N_1/N_0$, N_0 = total number of molecules in the liquid phase initially, and R_0 being the initial ratio of heavy to light isotopes.

Equation (3.4) describes the ratio of heavy to light isotopes in the liquid as a function of the volume fraction f , when the evaporation proceeds in a system under equilibrium conditions. This is analogous to the Rayleigh distillation process and is also called the Rayleigh distillation formula.

Reverse Rayleigh process - condensation

In the reverse process, let the removal of $H_2^{16}O$ by condensation from the gaseous phase (in equilibrium with liquid phase) be dN_g and $d(R_g N_g)$ the corresponding removal of $H_2^{18}O$. The removal of $H_2^{18}O$ from the liquid phase will be $R_1 \cdot dN_g$.

$$\text{Thus, } d(R_g N_g) = R_1 \cdot dN_g = \alpha \cdot R_g \cdot dN_g$$

$$\text{or } \frac{dR_g}{R_g} = \frac{dN_g}{N_g} (\alpha - 1)$$

Integrating from R_0 to R_g and N_0 to N_g we get

$$\ln \frac{R_g}{R_0} = \ln \frac{N_g}{N_0} (\alpha - 1)$$

$$\text{or } R_g = R_0 f^{(\alpha-1)} \quad (3.5)$$

Equation (3.5) gives the isotopic change in the gaseous phase as condensation proceeds and is called the Rayleigh condensation formula.

Now, from the definition of δ we have that

$$\delta = \frac{(R-R_0)}{R_0} = \frac{R}{R_0} - 1$$

$$\text{or } \frac{R}{R_0} = 1 + \delta$$

(Note that δ is not in ‰ and $\ln(1 + \delta) \approx \delta$.)

In terms of δ , eqs (3.4) and (3.5) take the form

$$\delta \approx \left(\frac{1}{\alpha} - 1 \right) \ln f \quad \text{for evaporation} \quad (3.4a)$$

$$\text{and } \delta \approx (\alpha - 1) \ln f \quad \text{for condensation} \quad (3.5a)$$

So far we have studied the case when evaporation or condensation proceeds in a system where equilibrium exists between the liquid and the gaseous phases. In nature, however, such ideal situations are seldom encountered. We now consider a case when an open water body without inflow or outflow (say a pan) is subjected to slow evaporation which results in isotopic fractionation.

3.3 Fractionation in an open water body evaporating in an atmosphere under constant relative humidity and temperature.

For the sake of simplicity, we can draw an analogy for the above system with an evaporating pan without any inflow or outflow. Since the atmospheric vapour also have a certain amount of ^{18}O , there will be an isotopic exchange between liquid and vapour. This exchange will be superimposed on the fractionation occurring purely due to evaporation and will modify the isotopic picture of the evaporating liquid mass.

Dansgaard (1961) and Craig et al. (1963) found in laboratory experiments that for evaporation into dry air the isotopic enrichment of water was higher than that expected from the simple Rayleigh distillation formula valid for equilibrium fractionation. Even when evaporation took place in an atmosphere containing water vapour, the enrichment was still found to be more than that of a system under liquid-vapour equilibrium (Rayleigh distillation). It was apparent that an excess separation or fractionation factor operates, which is greater

than the equilibrium fractionation factor α . Further, for evaporation into moist air, the heavy isotopic content of remaining water approaches a limiting value in the later stages of dessication, Craig et al. (1963).

The process of natural evaporation was modelled by Craig and Gordon (1965). The model assumes that the liquid-vapour interface is bounded on either side (in each phase) by a laminar layer, in which the transport is predominantly governed by molecular diffusion. Beyond these laminar layers, there is a region dominated by turbulence. This was shown experimentally by Merlivat and Coantic (1975), who found that the mass transfer in the region just above the water-air interface is dominated by molecular diffusion. From the kinetic theory of gases, Craig and Gordon (1965) estimated D_i/D for $H_2^{18}O/H_2^{16}O = 0.969$ and for $HD^{16}O/H_2^{16}O = 0.983$, where D refers to the molecular diffusivity and subscript i to the heavy components (^{18}O or D). Experimental values of these ratios reported by Ehhalt and Knott (1965) are 0.971 ± 0.001 and 0.985 ± 0.003 , respectively. Merlivat (1978) in two separate experiments found the corresponding values to be 0.9723 ± 0.0007 and 0.9755 ± 0.009 , taking into consideration not only the isotopic masses but also the isotope effect on the molecular diameters of the water molecules, i.e., $H_2^{18}O$, $H_2^{16}O$, and $HD^{16}O$.

The present treatment follows in a simplified form the same assumptions as of Craig and Gordon (1965).

- Let $N_l =$ total number of molecules of the lighter component ($H_2^{16}O$) in water
- $N_g =$ total number of molecules of the lighter component ($H_2^{16}O$) in atmospheric vapour
- $N^*_l =$ number of molecules of the heavy component ($H_2^{18}O$) in water
- $N^*_g =$ number of molecules of the heavy component ($H_2^{18}O$) in atmospheric vapour
- $F_{lg} =$ flux of lighter component from liquid to gaseous phase
- $F^*_{lg} =$ flux of heavier component from liquid to gaseous phase
- $F_{gl} =$ flux of lighter component from gaseous to liquid phase
- $F^*_{gl} =$ flux of heavier component from gaseous to liquid phase

R_l & R_g = the ratios of the heavy to the light component in water and gaseous phase (i.e. atmosphere), respectively

$E^* = F_{lg}^* - F_{gl}^*$, is the net flux of heavy component from liquid to gaseous phase

$E = F_{lg} - F_{gl}$, is the net flux of light component from liquid to gaseous phase

$R = E^*/E$, the ratio of heavy to light component in the net flux from liquid to gaseous phase, then

$$N_l^* = R_l N_l \quad \text{and} \quad N_g^* = R_g N_g$$

As evaporation proceeds the change in the heavier component in liquid phase dN_l^* is given by

$$d(N_l^*) = E^*/E \cdot d(N_l) = d(R_l N_l)$$

$$\text{or } d(R_l \cdot N_l) = R \cdot dN_l$$

$$\text{or } \frac{dR_l}{R_l} = \frac{dN_l}{N_l} \left(\frac{R}{R_l} - 1 \right)$$

$$\text{or } \frac{d(\ln R_l)}{d(\ln N_l)} = \left(\frac{R}{R_l} - 1 \right) \quad (3.6)$$

Similarly it can be shown that the change in the heavier component in the gaseous phase is described by

$$\frac{d(\ln R_g)}{d(\ln N_g)} = \left(\frac{R}{R_g} - 1 \right) \quad (3.7)$$

If the relative humidity is h , then the flux from gaseous to liquid phase can be expressed as

$$F_{gl} = h F_{lg}, \text{ when } h = 1, F_{gl} = F_{lg}$$

and there is no net flux across the interface. On the other hand, if $h = 0$ then $F_{gl} = 0$, and there is no flux from gaseous to liquid phase and evaporation proceeds in vacuum, while for $h \geq 1$, the gaseous phase is condensing.

The flux F_{lg} is directly proportional to N_l the total number of molecules in the liquid phase, hence

$$F_{lg} = K_{lg} N_l \quad \text{similarly} \quad F_{gl} = K_{gl} N_g,$$

$$F_{lg}^* = K_{lg}^* R_l N_l \quad \text{and} \quad F_{gl}^* = K_{gl}^* R_g N_g$$

K_{lg}^* and K_{lg} are the resistances to the flow of the heavy and light components from the liquid to the gaseous phase respectively; K_{gl}^* and K_{gl} being the corresponding resistances from gaseous to liquid phase.

$$\text{Now } E^* = F_{lg}^* - F_{gl}^* = K_{lg}^* \cdot R_l \cdot N_l - K_{gl}^* \cdot R_g \cdot N_g$$

$$\text{or } E^* = \frac{K_{lg}^* R_l F_{lg}}{K_{lg}} - \frac{K_{gl}^* R_g h F_{lg}}{K_{gl}} \quad (3.8)$$

From the definition of E we have

$$E = (1 - h) F_{lg}$$

Substituting

$$r_{lg} = \frac{K_{lg}^*}{K_{lg}} \quad \text{and} \quad r_{gl} = \frac{K_{gl}^*}{K_{gl}}$$

r_{lg} is the ratio of the resistances of the interface to molecules of the heavy and light components from liquid to gaseous phase. r_{gl} can be similarly defined.

We have

$$R = \frac{E^*}{E} = \frac{(r_{lg} \cdot R_l - r_{gl} \cdot R_g \cdot h)}{(1 - h)} \quad (3.9)$$

Equation (3.9) defines R , which is the ratio of the heavy to the light component in the net evaporate, under a constant humidity, h .

Now, in analogy with phase transition eq.(3.2), i.e. $R_l = \alpha R_g$, we may write

$$R_l = \frac{r_{gl}}{r_{lg}} \cdot R_g, \quad \text{which is justified since } r_{gl} > r_{lg}.$$

During evaporation then

$$\alpha = r_{gl}/r_{lg}$$

$$\text{and } R = \frac{E^*}{E} = \frac{\left(\frac{1}{\alpha} \cdot R_l - h \cdot R_g\right) r_{gl}}{(1 - h)} \quad (3.10)$$

where R is the ratio of heavy to light component fluxes through the interface. Equation (3.10) is similar to one obtained by Gat (1981), which is a simplification of Craig and Gordon (1965). Here $r_{g1} = \rho/\rho_1$ of Gat and has a similar meaning.

Equation (3.10) can be written in terms of the δ values. Substituting $r_{g1} = 1/\beta$ and R , R_1 , R_g as their corresponding δ values, for example $R_1 = R_{STD}(1 + \delta_1)$, and so forth, we get

$$\delta_{\text{evaporate}} = \frac{\frac{1}{\alpha} (1 + \delta_1) - h(1 + \delta_g)}{(1 - h)\beta} - 1 \quad (3.11)$$

It will be shown later that $\delta_{\text{evaporate}}$ (i.e. δ_E) must be determined accurately to predict the changes in the δ value of a water body evaporating in natural conditions. In such situations α , δ_g and h are always changing. Furthermore, an optimum value of β is also required.

Using eq.(3.10) we can derive expressions for several cases.

Case I: Dynamic equilibrium

In this situation, the liquid and vapour are in dynamic equilibrium, the net evaporation is zero, $E = E^*$ and $h = 1$, using eq.(3.10) we get

$$\frac{1}{\alpha} R_1 - R_g = 0$$

$$\text{or } R_1 = \alpha R_g$$

which as expected is also the expression for the phase transition equation.

Case II: Evaporation in vacuum

$h = 0$ in this case and eq.(3.10) reduces to

$$R = \frac{R_1}{\alpha} r_{g1}$$

substituting R in eq.(3.6)

$$\frac{d(\ln R_1)}{d(\ln N_1)} = \left(\frac{r_{g1}}{\alpha} - 1 \right)$$

This equation has the same form as Rayleigh's distillation formula, but for the extra term r_{g1} as the system is not in equilibrium.

However, our intentions are to describe the changes in δ values of a liquid phase undergoing evaporation under a certain humidity h (so far only the isotopic ratio R of the net evaporate has been obtained), we substitute R from eq.(3.10) in eq.(3.6), thus

$$\begin{aligned} \frac{d(\ln R_1)}{d(\ln N_1)} &= \frac{(\frac{1}{\alpha} \cdot R_1 - h \cdot R_g) r_{g1}}{(1 - h) \cdot R_1} - 1 \\ &= \frac{r_{g1} (\frac{1}{\alpha} - h \frac{R_g}{R_1})}{(1 - h)} - 1 \end{aligned} \quad (3.12)$$

Now we define a new term, $\Delta\epsilon$, such that

$$\Delta\epsilon = (1 - h) \left(\frac{1}{r_{g1}} - 1 \right)$$

This is exactly the same as $\Delta\epsilon$ of Craig and Gordon (1965), only r_{g1} replaces their ρ/ρ_i . $\Delta\epsilon$ in both cases is the kinetic contribution to the isotopic fractionation or in a sense is equivalent to the excess separation or fractionation factor discussed earlier.

$$\text{Thus } r_{g1} = \frac{1 - h}{1 - h + \Delta\epsilon}$$

and substituting r_{g1} in eq.(3.12) we get

$$\begin{aligned} \frac{d(\ln R_1)}{d(\ln N_1)} &= \frac{(\frac{1}{\alpha} - h \frac{R_g}{R_1})}{(1 - h)} \cdot \frac{(1 - h)}{(1 - h + \Delta\epsilon)} - 1 \\ &= \frac{\frac{1}{\alpha} - h \frac{R_g}{R_1}}{1 - h + \Delta\epsilon} - 1 \end{aligned} \quad (3.13)$$

$$\text{Substituting } \beta = \frac{1}{r_{g1}} = \frac{1 - h + \Delta\epsilon}{1 - h}$$

such that $1 - h + \Delta\epsilon = (1 - h)\beta$, eq.(3.13) takes the form

$$\frac{d(\ln R_1)}{d(\ln N_1)} = \frac{\frac{1}{\alpha} - h \frac{R_g}{R_1}}{(1 - h)\beta} - 1 \quad (3.14)$$

Using eq. (2.1) where $\delta_1 = R_1/R_{SMOW} - 1$

and $R_1 = R_{SMOW}(1 + \delta_1)$, $R_g = R_{SMOW}(1 + \delta_g)$

$$\text{also } d(\ln R_1) = \frac{d \delta_1}{(1 + \delta_1)}$$

Equation (3.14) takes the new form as

$$d(\delta_1) = \frac{\frac{1}{\alpha} (1 + \delta_1) - h(1 + \delta_g) - \beta(1 - h)(1 + \delta_1)}{\beta(1 - h)} d(\ln N_1) \quad (3.15)$$

Thus eq.(3.15) describes the change in δ values of a water body evaporating under constant humidity h and constant temperature.

To predict $d(\delta_1)$, δ_1 of the water body and δ_g of the atmospheric vapour must be known as well as α at the prevailing temperature, the humidity h and β . The value of β can be obtained from eq.(3.15), provided the atmospheric conditions, i.e. h , δ_g , and temperature, remain constant. Under natural conditions, β can only be averaged during a certain time period using average values of h , δ_g , and temperature. Gat (1970) found experimentally that β varied from 1.103 to 1.106. He further concluded that during night, when winds are calmer, the character of the diffusive layer near the interface is more laminar, and consequently β is higher.

Consider a case when the water body has evaporated long enough and reaches an isotopic stationary state, i.e. no further changes occur in its $\delta^{18}\text{O}$ content. This implies that $d(\delta_1) = 0$

Equation (3.15) then takes the form

$$(1 + \delta_1) \left(\frac{1}{\alpha} - \beta(1 - h) \right) = h(1 + \delta_g)$$

$$\text{or } \delta_1 = \frac{h(1 + \delta_g)}{\frac{1}{\alpha} - (1 - h)\beta} - 1 \quad (3.16)$$

Further evaporation will not cause any change in the δ value of remaining water provided atmospheric conditions remain constant.

It has been observed that the relative humidity of the atmosphere determines how rapidly the evaporating body approaches stationarity. On the other hand, small fluctuations in δ values of the atmospheric vapour are relatively unimportant.

3.4 Fractionation in an open water body evaporating freely with an inflow (constant volume conditions) in an atmosphere.

As an extension to the previous case where the pan was evaporating to dryness, here we consider a pan such that the evaporation losses are equal to an inflow and constant volume conditions prevail.

Starting again from the first principles, let

S_1 = the mass of liquid (water) in the pan

F_{11} = the inflow of water from the reservoir

R_1, R_g, R_{11} = the ratios of heavy to light components in the pan, atmosphere and inflow, respectively.

From the conditions of mass balance we have

$$\frac{dS_1}{dt} = -F_{1g} + F_{g1} + F_{11} \quad (3.17)$$

and from the isotope balance

$$\frac{d}{dt} (S_1 R_1) = S_1 \frac{dR_1}{dt} + R_1 \frac{dS_1}{dt} = -F^*_{1g} + F^*_{g1} + F^*_{11}$$

When water in the pan has reached isotopic steady state, then $R_1 = \text{constant}$ and $dR_1/dt = 0$

$$\text{and } R_1 \frac{dS_1}{dt} = -F^*_{1g} + F^*_{g1} + F^*_{11} \quad (3.18)$$

Now from the previous section

$$F^*_{lg} = \frac{K^*_{lg}}{K_{lg}} \cdot R_l F_{lg} = r_{lg} \cdot R_l \cdot F_{lg}$$

$$\text{and } F^*_{gl} = r_{gl} \cdot R_g \cdot F_{gl}, \quad F^*_{ll} = R_{ll} \cdot F_{ll}$$

From eqs (3.17) and (3.18), after substituting for F^*_{gl} , F^*_{lg} and F^*_{ll} , we get

$$- R_l F_{lg} + R_l F_{gl} + R_l F_{ll} + r_{lg} R_l F_{lg} - r_{gl} R_g F_{gl} - R_{ll} F_{ll} = 0$$

$$\text{or } R_l F_{lg}(-1 + r_{lg} + h) = h R_g r_{gl} F_{gl} + F_{ll}(R_{ll} - R_l) \quad (3.19)$$

From the previous section, we have seen that $r_{lg}/r_{gl} = 1/\alpha$ and $1/r_{gl} = \beta$

Dividing eq.(3.19) by r_{gl} , we get

$$R_l F_{lg}[-(1 - h)\frac{1}{r_{gl}} + \frac{1}{\alpha}] = h R_g F_{gl} + \beta(R_{ll} - R_l)F_{ll} \quad (3.20)$$

Equation (3.20) is a general form and can be reduced to special cases.

Case I: When there is no inflow, i.e. the pan is evaporating to dryness, then $F_{ll} = 0$ and eq.(3.20) takes the form

$$R_l(\frac{1}{\alpha} - (1 - h)\beta) = h R_g$$

$$\text{and } R_l = \frac{h R_g}{(\frac{1}{\alpha} - (1 - h)\beta)}$$

In terms of δ values we can write the above equation as

$$\delta_l = \frac{h(1 + \delta_g)}{\frac{1}{\alpha} - (1 - h)\beta} - 1$$

This expression giving the isotopic composition of the liquid when it has attained a steady state is the same as eq.(3.16). However, we are interested in determining the isotope composition of the pan water when there is an inflow and the liquid attains a steady state.

Case II: inflow = evaporation, i.e.

$$F_{11} = E = (1 - h) F_{lg}$$

Then rearranging eq.(3.20) and substituting for F_{11} , we get

$$R_1 \frac{1}{\alpha} = h R_g + \beta R_{11} - \beta h \cdot R_{11}$$

and in terms of δ values

$$\delta_1 = [h(1 + \delta_g) + \beta(1 - h)(1 + \delta_{11})]\alpha - 1 \quad (3.21)$$

Equation (3.21) gives the δ value of the pan water when isotopic steady state has been reached, δ_{11} being the δ value of the inflow to the pan.

3.5 Fractionation in an open water body from the mass and isotopic balance.

Given the isotopic composition of the net evaporate, the isotopic changes of a well mixed water body can also be obtained from water and isotope balance, in a slightly different way than previously described. The present treatment in its general form is more useful for hydrological purposes.

If E is the rate of evaporation, I is the inflow, Q is the outflow then the water balance is

$$\frac{dS}{dt} = I - Q - E \quad (3.22)$$

From isotope balance we have

$$\frac{d(S \cdot R_S)}{dt} = I R_I - Q R_Q - E R_E \quad (3.23)$$

where S = mass of the water body
 t = time

and R_S, R_I, R_Q & R_E = isotopic ratios of the water body, inflow, outflow and the evaporate respectively.

Integration of eq.(3.22) yields

$$S = S_0 - \int_0^t (E + Q - I) dt \quad (3.24)$$

where S_0 = mass of water at $t = 0$

Equations (3.22), (3.23) and (3.24) give

$$\frac{dR_S}{dt} = \frac{E(R_S - R_E) - I(R_S - R_I) + Q(R_S - R_Q)}{S_0 - \int_0^t (E + Q - I)dt} \quad (3.25)$$

and in the δ notation

$$\frac{d\delta_S}{dt} = \frac{E(\delta_S - \delta_E) - I(\delta_S - \delta_I) + Q(\delta_S - \delta_Q)}{S_0 - \int_0^t (E + Q - I)dt} \quad (3.26)$$

If the amount of inflows, outflows and their corresponding δ values are known, eq.(3.26) can be solved numerically for δ_S , using δ_E from the preceeding time step using eq.(3.11). It is readily seen that the above equation can be easily reduced to special cases such as

- a) isolated water body, i.e. no inflow or outflow
- b) water body with inflow but no outflow
- c) water body with inflow and outflow.

For the sake of brevity and simplicity, only case (a) is treated here.

Case (a): Since inflow and outflow are zero, then $I = 0$, $Q = 0$, $\delta_I = 0$ and $\delta_Q = 0$, and eq. (3.26) takes the form

$$\frac{d\delta_S}{dt} = \frac{E(\delta_S - \delta_E)}{S_0 - \int_0^t E \cdot dt} \quad (3.27)$$

When isotopic stationarity is achieved, $\frac{d\delta_S}{dt} = 0$ and $\delta_S = \delta_E$.

Substituting δ_E from eq.(3.11) and writing δ_1 instead of δ_S which is the δ value of the water body, we get

$$\delta_1 = \frac{\frac{1}{\alpha} (\delta_1 + 1) - h(\delta_g + 1) - \beta(1 - h)}{(1 - h)\beta}$$

Rearranging the terms in the above equation, we get

$$\delta_1 = \frac{h(\delta_g + 1)}{\frac{1}{\alpha} - \beta(1 - h)} - 1$$

which is exactly the same as eq.(3.16) derived earlier from the first principles. For practical purposes, the use of eq.(3.26) is quite advantageous because of the relative ease in reducing it to several special conditions of inflows, outflows and their various combinations.

4 PAN EVAPORATION EXPERIMENTS TO STUDY THE WATER BALANCE OF OPEN WATER BODIES

4.1 Introduction

It has been seen in the previous sections that the basic principles of fractionation of stable isotopes (^{18}O and D) between the liquid and vapour phases of water are rather well known. Many attempts have been made to study the water balance of lakes using stable isotopes. Consider the mass and isotope balance equations (3.22 and 3.23) of an open water body. Any two terms in the mass balance can be obtained provided all the isotope values are either measured or estimated. Generally, inflow to and evaporation from a lake are of greater interest. This requires a prior knowledge of δ_E (the lake evaporate) which cannot be determined experimentally.

As discussed earlier, δ_E can be estimated either from the Craig and Gordon model (Craig and Gordon, 1965) or from eq.(3.11). This requires accurate measurements of relative humidity (h), the fractionation factor α , the parameter β and δ values of atmospheric moisture and lake water. Zimmermann and Ehrlert (1970) suggested that the use of the Craig and Gordon model may lead to inaccuracy in δ_E estimates because of the difficulty in measuring relative humidity with sufficient accuracy. Dinger (1968) made use of an "index lake" (a lake whose water balance terms were accurately known) to estimate δ_E and used it to study the water balance of nearby lakes.

In a much simpler approach, Friedman and Redfield (1971) attempted to study the water balance of the lower Grand Coulee lakes using an estimated effective fractionation factor, circumventing the estimation of δ_E . Gat (1970) used the Craig and Gordon model to estimate δ_E from pan evaporation experiments. He reported an error of about 10% in the estimation of inflow to the lake Tiberias. Gat's success in the above study was due to that he did not use a constant value of $\Delta\epsilon$ (the kinetic separation factor) during the observation period. Instead $\Delta\epsilon/(1-h)$ was varied from 13 to 16‰ to give the best theoretical fit to isotopic fractionation observed in the pan water. Welhan and Fritz (1977) and Allison et al. (1979) also tried to estimate δ_E using data from pans evaporating to dryness. It was found that δ_E can be determined with sufficient accuracy, only when the meteorological conditions (especially relative

humidity, h) are fairly constant and the evaporating volume approaches an isotopic steady state. Since constant weather situations rarely occur in nature, Allison and Leaney (1982) tried to overcome the problem of isotopic steady state attainment by using constant volume or constant feed pans. Using normalized relative humidity, they found a close agreement between the observed mean values of h and δ_a (δ value of atmospheric moisture) and their estimated values when the pans approached an isotopic steady state, evaporation time being greater than 500 hours. The above studies were hampered by the large variations of relative humidity and the assumption of constant conditions of evaporation. Further, the estimated values of δ_E were valid for the period when pan water attained isotopic steady state.

In recent years, apart from the studies on the water balance of lakes, stable isotopes have also become important tools for investigations of the process of stream runoff. The contribution to streamflow from various reservoirs as well as transit times of water in the basins have been quantified, Fritz et al. (1976), Herrmann and Stichler (1983) and Rodhe (1984). In such studies the stable isotopes have been treated as conservative tracers from the moment of rainfall or snowmelt to the moment of stream discharge from the basin. No attention has been paid to the possible isotope changes occurring due to the fractionation by evaporation and molecular exchange with the atmosphere. Theoretical considerations from Swedish basins also show that in certain situations, enrichment in ^{18}O may occur during surface water flow, the magnitude of which cannot be ignored, Rodhe (1985).

4.2 Pan evaporation experiments at Uppsala

It is obvious from the previous discussions that whenever isotopes are to be used for lake water balance or runoff studies, the isotopic fractionation of surface water has to be quantified. In other words, the δ value of the evaporate (δ_E) from a water mass has to be determined as accurately as possible. With this objective in mind a study of isotopic fractionation in evaporating pans was conducted in Uppsala during 1981-82.

The main aim of the experiment was to accurately predict the isotope changes of pan water during all the stages of evaporation unhampered by the limiting conditions of uniform relative humidity and the approach to isotopic steady state of pan

water. In order to achieve this, the fractionation factor (α) was varied with temperature and the kinetic separation factor was adjusted with relative humidity (h) using the experimental pan data. From the pan water's mass and isotope balance, the experimental value of δ_E was determined and compared with the computed value of δ_E (using eq.3.11). This also provided a check of the validity of eq.(3.11) for describing the fractionation in nature.

In the present study, pans with constant volume (i.e. having an inflow equal to the evaporation loss) and pans evaporating to "dryness" (without inflow) were used.

For pans evaporating to dryness eq.(3.27) is used, and for constant volume pans (with inflow = evaporation) the expression is

$$\frac{d\delta_S}{dt} = \frac{E(\delta_S - \delta_E) - I(\delta_S - \delta_I)}{S_0} \quad (4.1)$$

As evaporation proceeds, pan water δ_S strives to reach an equilibrium with the atmosphere. In order to distinguish this equilibrium value from the thermodynamic equilibrium ($h = 1.0$) it will henceforth be called "the steady state value". For a pan evaporating to dryness the steady state value is obtained when $\delta_S = \delta_E$ in eq.(3.27). Manipulation of eq.(3.11) when $\delta_S = \delta_E$, Rodhe (1987), gives

$$\delta_{ss} - \delta_a = (1 + \delta_a) \frac{\frac{1}{\alpha} - h - \beta(1 - h)}{\beta(1 - h) - \frac{1}{\alpha}} \quad (4.2)$$

Equation (4.2) gives the steady value δ_{ss} of pan water in the ideal case when the relative humidity, h , and the ^{18}O content of the atmospheric moisture, δ_a , are constant. A graph of $\delta_{ss} - \delta_a$ versus relative humidity is shown in Fig.(4.1). The diagram also picturises the condition for enrichment or depletion during evaporation. When $(\delta_{ss} - \delta_a)$ for a certain h are below the full-drawn curve enrichment will take place, and when they are above the curve, evaporation will cause depletion. Depletion, as discussed here, can occur when δ_a is quite low and h quite high. Such situations can be encountered in Sweden during autumn periods. A practical example of this is given later in the text. As is obvious from Fig.(4.1), δ_{ss} is very sensitive to variations in relative humidity.

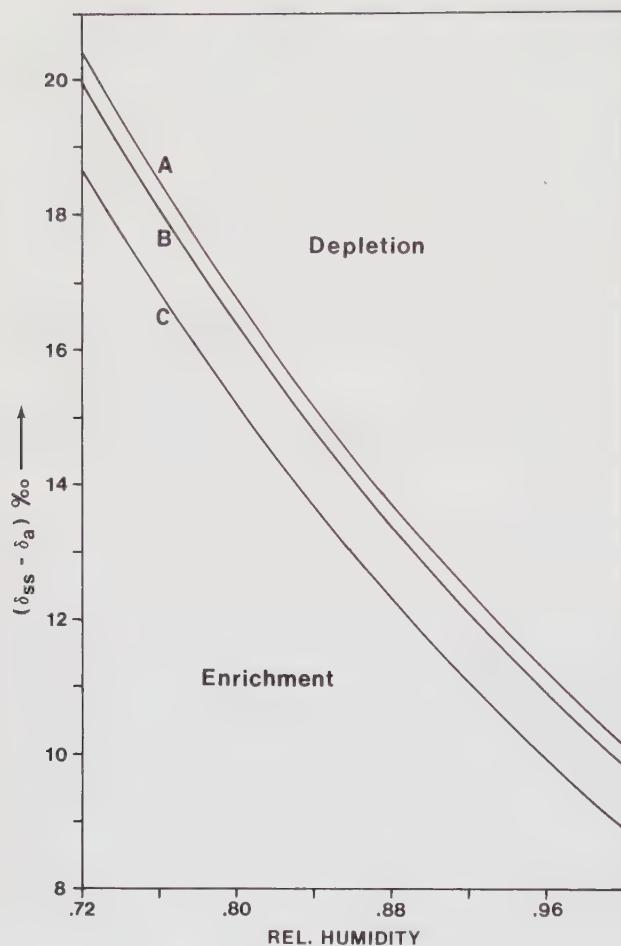


Fig.(4.1) Isotopic difference between the "steady state value" of pan water (δ_{ss}) and atmospheric vapour (δ_a) versus relative humidity. Curve A is for $\alpha = 1.0103$, curve B for $\alpha = 1.010$ and curve C for $\alpha = 1.0090$.

4.3 Experimental set-up

To study the isotopic fractionation of water evaporating under natural conditions, cylindrical evaporation pans (diam. 37.5 cm) were filled with water of known δ value. The depth of water was varied from 30 to 95 mm. In some pans, called decreasing volume pans, there was no inflow, i.e. the volume of water decreased by evaporation. In others, called constant volume pans, inflow was regulated by a Mariotte's bottle, keeping constant water level in the pans.

The first phase of the experiment was started in July 1981. The pans were kept under a roof 2.5 m high, covered from three

sides by a wire mesh having 4 cm^2 holes and closed from the back by a wall.

The second phase of the experiment was started in June 1982 on a roof-top. The pans were kept on a wooden bench and were covered at the top and the sides by transparent sheets of polythene as a protection from rain. The transparent cover, mounted on a wooden frame, was designed to allow a free flow of wind from the bottom, but was shielded from birds by a plastic mesh of 9 mm^2 holes. 5 ml water was periodically removed from the pans to determine δ_g . This volume corresponds to 0.045 mm evaporation from the pan compared to about 2 mm daily evaporation and has no significant effect on δ_g . Temperature and relative humidity of air were continuously recorded in the covered area, while in 1981 observations from a weather station 3 km away from the site were used.

Sampling during both phases varied from one to three days depending upon the rate of evaporation from the pans. The samples were analysed on a ratio type mass-spectrometer. The error in measurements is about $\pm 0.1\%$.

4.3.1 Monitoring of ^{18}O in atmospheric vapour

In order to trace the short term variations of ^{18}O in atmospheric vapour, a suitable method ensuring a continuous sampling of vapour is necessary. It is also required that a given mass of vapour should be condensed completely, since any loss of vapour will cause an isotopic fractionation of the condensed mass. With this in mind, sampling was performed in the following way. Air was sucked at a rate of 60 l/h by a membrane pump through two glass traps connected in series and continuously kept at -60°C by an electric compressor, Fig.(4.2). After 24 hours interval, the glass traps were taken out and allowed to thaw, liquid water from both traps was mixed thoroughly, though the amount of water in the second trap was less than 0.1% of the first.

The residual saturation vapour pressure of water is $\approx 1 \text{ Pa}$ at -60°C . Thus, theoretically, some vapour will suffer only partial condensation leading to a small enrichment of the condensed mass. In order to test the magnitude of such an error, dry nitrogen was bubbled through 15 g of water of known δ value. The stream of nitrogen and moisture was passed through the same cold traps (kept at -60°C) at a rate of 60 l/h. It took almost

24 hours to bubble 15 g water to dryness, which is also the time required for the regular air sampling by suction. The glass traps were thawed and weighed, and it was found that there was practically no loss of vapour during several trials. The $\delta^{18}\text{O}$ of the recovered water deviated from its true value by $\pm 0.1\text{‰}$, which is also the measurement error of the mass-spectrometer. From the above checks, it was concluded that no correction is needed for the $\delta^{18}\text{O}$ of recovered moisture.

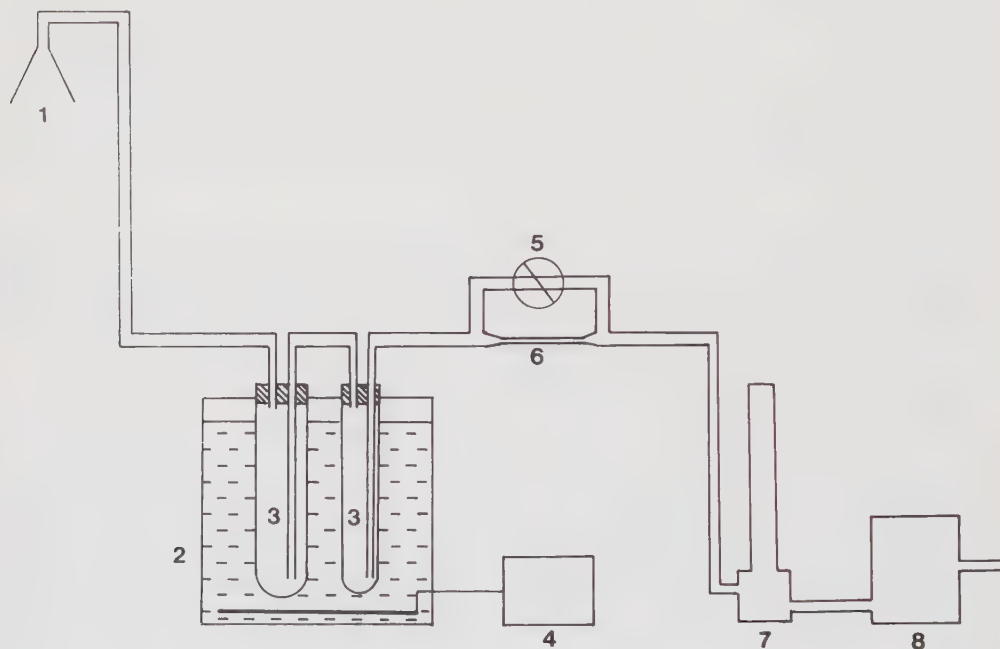


Fig.(4.2) Apparatus for removal of moisture from air for isotopic monitoring. 1 = air intake funnel, 2 = dewar container filled with alcohol at -60°C , 3 = glass traps, 4 = compressor for cooling alcohol, 5 = regulator for air flow, 6 = capillary, 7 = flow meter and 8 = membrane pump.

Cooling of the traps by a compressor was preferred to the usual freezing mixtures (dry ice + alcohol, etc.) as they require a constant and laborious care. They also suffer from temperature fluctuations. Thoma et al.(1979) have reported yet another method based on absorption of moisture on molecular sieves. This method is amenable to deuterium analysis, but fails in the case of ^{18}O , as the sieve's oxygen atoms begin to exchange with ^{18}O atoms of the vapour.

The sampling for ^{18}O was started in Uppsala in July 1981 on a daily basis during summer months and 48 hours basis or more during winter.

4.4 Results and discussions

The pan water $\delta^{18}\text{O}$ values have been computed using average values of h (relative humidity), δ_a ($\delta^{18}\text{O}$ of air) and E (actual evaporation from the pans) during successive observations, from the beginning to the end of the experiment. The time period between the observations generally varied from 2 to 3 days or more, depending upon the depth of water in the pan. In the computations, α is not a constant and varies with the mean temperature prevailing in the observation periods. The value of β has been chosen as 1.016. Here β is equivalent to $(1 + \Delta\epsilon/(1-h))$ used by Gat (1970). Instead of the normalized relative humidity, the relative humidity of air has been used in the calculations because the temperature of the pan water was not recorded.

Equations (3.27) and (4.1) have been used to compute δ values of pans evaporating to dryness and constant volume pans respectively. Computed δ values of pan 1, Fig.(4.3), and pan 5, Fig.(4.4), show that computations with $\beta = 1.016$ have a better agreement with the observed δ values than when β is chosen as 1.014. For other pans also, better agreement between computed and observed δ values was obtained using $\beta = 1.016$. Thus the choice of $\beta = 1.016$ is considered to be more realistic for Swedish conditions. This implies that for Uppsala ($\Delta\epsilon/(1-h)$) was 16‰ (since $\beta = 1 + \Delta\epsilon/(1-h)$ in eq.3.11). As mentioned earlier, Gat (1970) also found $\Delta\epsilon/(1-h)$ to vary between 13 and 16‰ in the Lake Tiberias region, while in a more humid climate (similar to Uppsala), Allison and Leaney (1982) obtained a best fit to observed pan δ values by varying $\Delta\epsilon/(1-h)$ from 16 to 17‰.

The observed and computed δ values of pan water are shown in Figs (4.3) to (4.7). A comparison between observed and computed values shows that the agreement is fairly good in almost all the cases. The initial periods of evaporation are well described by the model, but towards the end of each experiment the computed values are generally lower than those observed. However, during 1981, pans 11 and 12 show a reverse trend, i.e. computed values are slightly higher than observed. This may be due to the fact that in 1981 relative humidity and daily mean temperature were not recorded at the site and are thus only

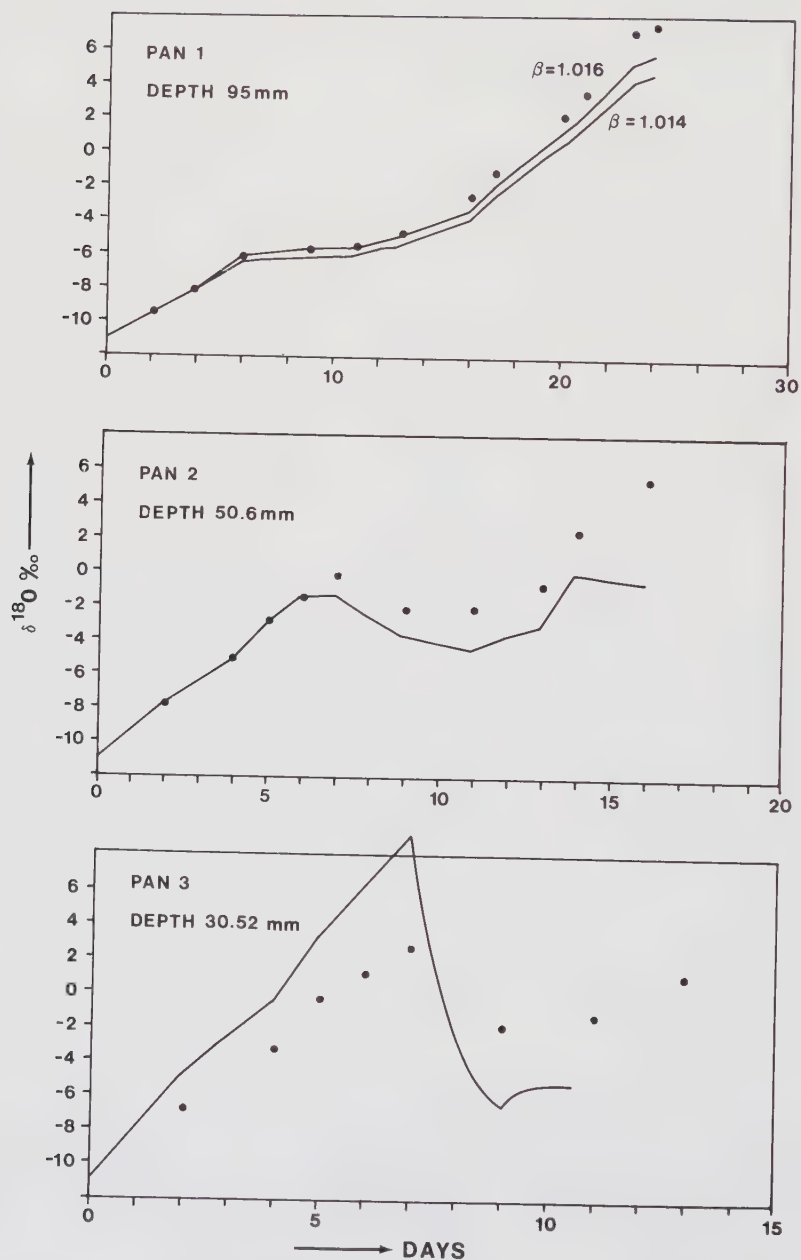


Fig.(4.3) Observed (dots) and computed (full line) δ values of pan water. Experiment started on 22 June 1982.

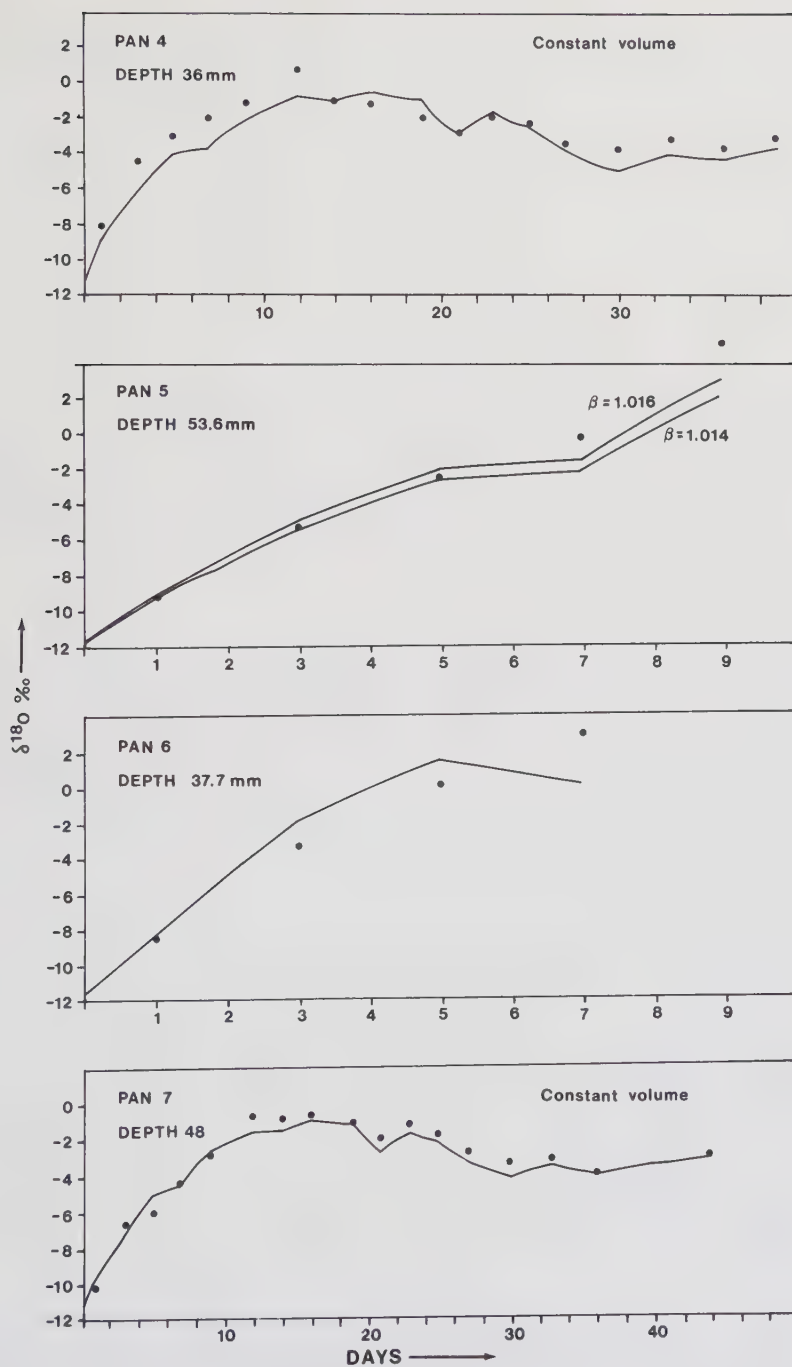


Fig.(4.4) Observed (dots) and computed (full line) δ values of pan water. Experiment started on 22 July 1982.

approximations of the true values. The deviations between the observed and computed values are also markedly high towards the end periods. This is due to the small volume of water remaining in the pan. The sinking of the water level below the rim of the pan inhibits turbulence and perhaps increases the thickness of the molecular diffusion dominated laminar layer above the liquid-air interface. Gat (1970) has also observed that with increasingly laminar character of the layer β is higher, resulting in a higher fractionation of the water. Since $\beta = 1.016$ is kept constant in the computation for all the periods, the computations thus are underestimates of fractionation when water volumes in the pans are greatly reduced. On the other hand, the constant volume pans show a good agreement between the observed and computed δ values throughout the length of the experiment (Fig.4.4, pans 4 and 7). For relatively smaller pans (Fig.4.3, pan 3, and Fig.4.5, pan 9), the relative deviations between observed and computed δ values are higher than those for larger pans towards the end periods.

It is sometimes observed that pan water gets depleted during the course of the experiments, followed by enrichment again in the later stages. For a pan evaporating to dryness, the so-called steady state value of ^{18}O of pan water given by eq.(4.2) is graphically illustrated in Fig.(4.1), i.e., the steady state value as a function of relative humidity. From Fig.(4.1) one can qualitatively check whether enrichment or depletion shall occur under a given value of $(\delta_{\text{pan}} - \delta_{\text{air}})$ versus the prevailing relative humidity.

For pan 2, Fig.(4.3), there is a depletion between the 7th to the 9th day. For this period $(\delta_{\text{pan}} - \delta_{\text{air}})$ is $\approx 19\text{‰}$ and $h_{\text{mean}} = 0.88$. Referring to Fig.(4.1), it is easily seen that for $\delta_{\text{pan}} - \delta_{\text{air}} = 19\text{‰}$ at $h = 0.88$, depletion should occur, which is in agreement with the experimental observations. The period between the 9th and the 11th day, showing little enrichment, is also in agreement with the graphical representation in Fig.(4.1). Similarly for pan 3, Fig.(4.3), $(\delta_{\text{pan}} - \delta_{\text{air}} = 24\text{‰}$; $h = 0.78$), depletion is observed especially between the 7th and the 9th day and is also confirmed from the graph, Fig.(4.1).

In general, for pans evaporating to dryness, all periods of enrichment or depletion observed experimentally are in agreement with the graphical representations in Fig.(4.1). However, Fig.(4.1) is only a qualitative representation of enrichment or depletion of pan water and does not quantify the amount of fractionation occurring.

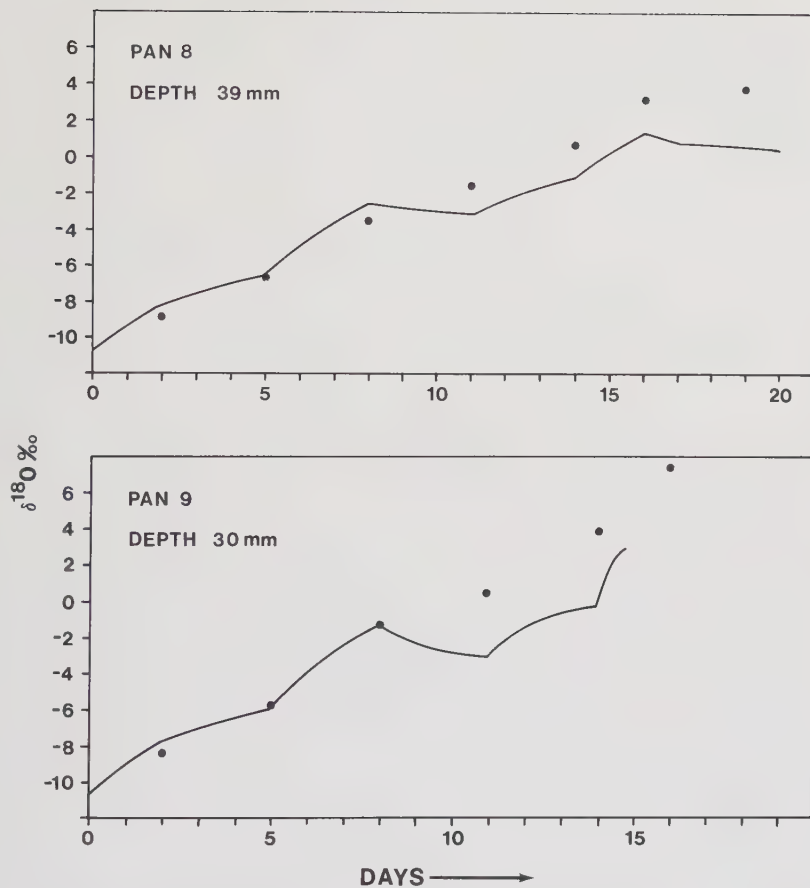


Fig.(4.5) Observed (dots) and computed (full line) δ values of pan water. Experiment started on 15 August 1982.

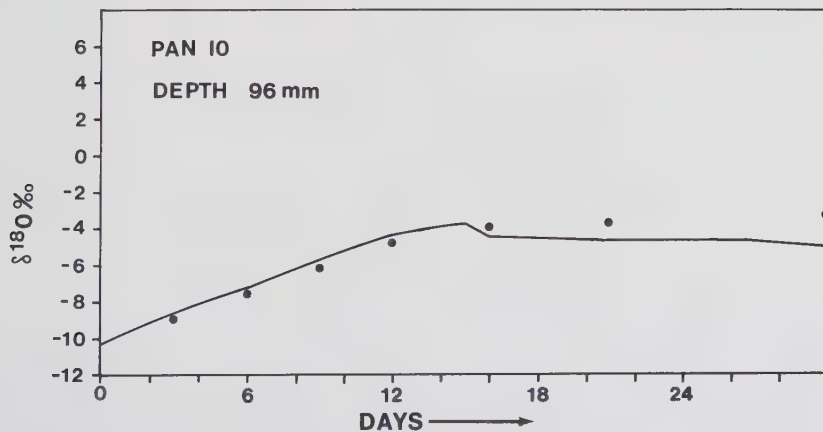


Fig.(4.6) Observed (dots) and computed (full line) δ values of pan water. Experiment started on 11 September 1982.

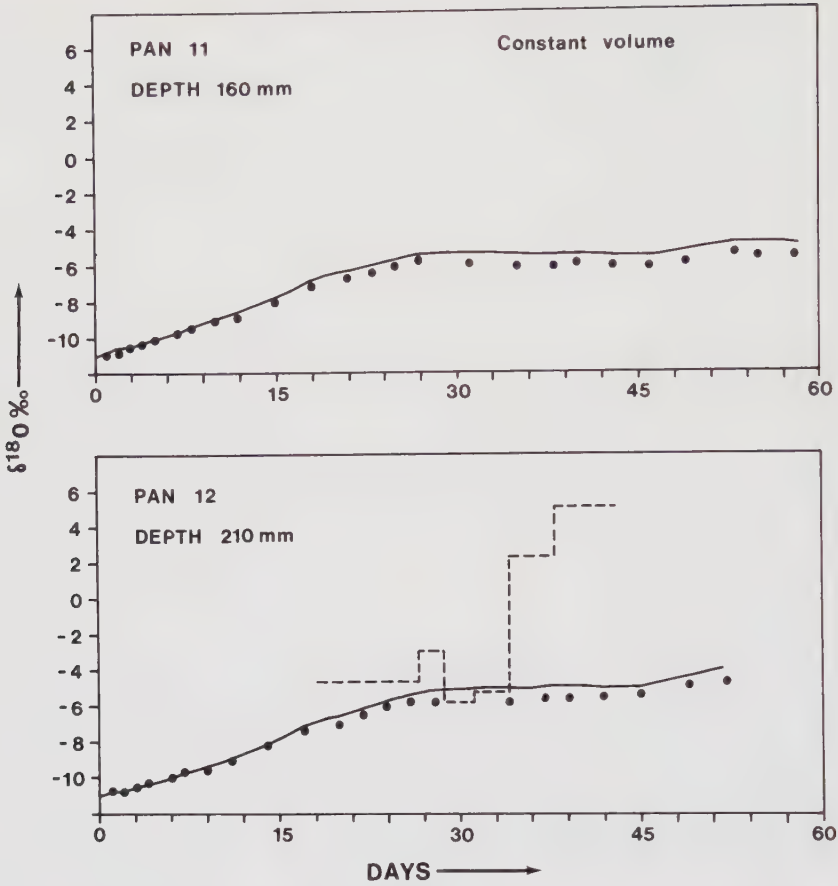


Fig.(4.7) Observed (dots) and computed (full line) δ values of pan water. Broken line for pan 12 shows the computed steady state value of pan water. Experiment started on 19 July 1981.

The δ value of the net evaporate (δ_E) during a time interval $(t-1)$ to (t) has been obtained experimentally from mass and isotopic balance of the pan water, i.e.:

$$\delta_{E(t-1,t)} = \frac{(\delta_{\text{pan}(t-1)} S(t-1) - \delta_{\text{pan}(t)} S(t))}{E(t-1,t)} \quad (4.3)$$

$S(t)$ is the amount of water in the pan at time "t".

The observed δ_E values for the total length of each experiment were compared with the calculated values. It is seen from Fig.(4.8) that the $\delta_{E(\text{cal})}$ and $\delta_{E(\text{obs})}$ follow each other quite closely. The scatter around a slope of 1 is influenced by small

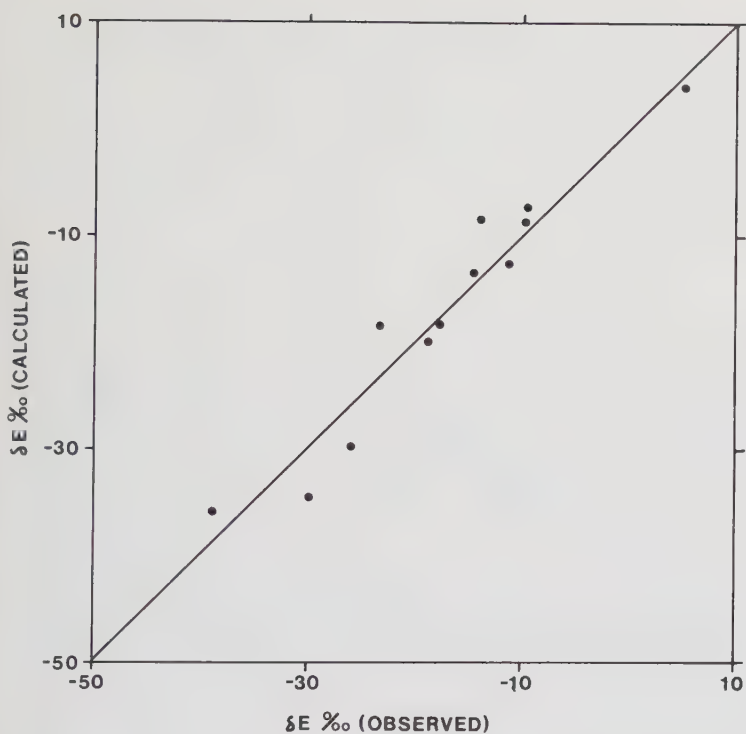


Fig.(4.8) The calculated and observed δ values of the pan evaporate (pan 1).

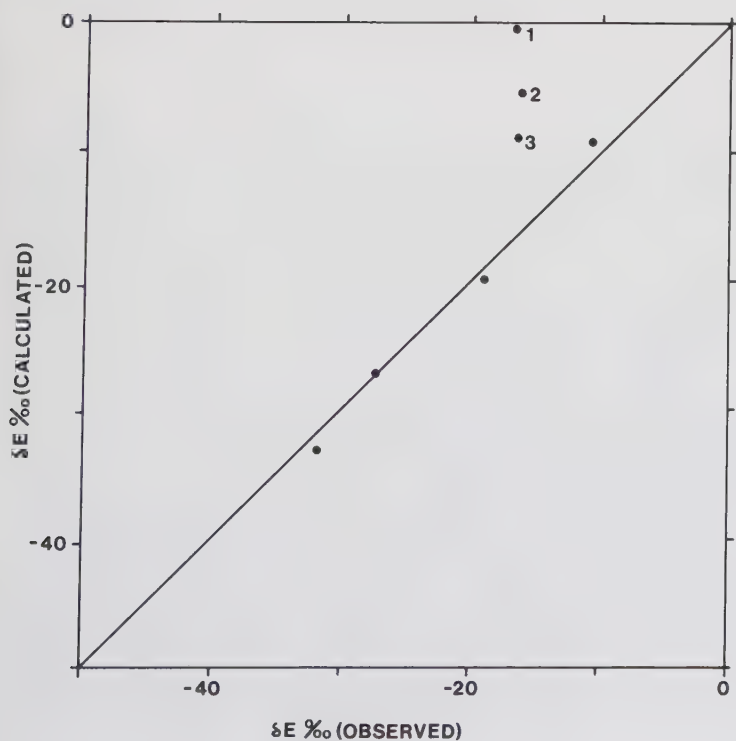


Fig.(4.9) The calculated and observed δ values of the pan evaporate (pan 2). Point 2 corresponds to relative humidity = 0.76, points 1 and 3 are for relative humidity 0.81 and 0.71 respectively

fluctuations in relative humidity and is illustrated in Fig.(4.9) for pan 2, where h (actual observed value 0.76, point 2) is varied by ± 0.05 . It is seen that a small change, 0.05, causes a considerable deviation from slope 1. Thus, it is clear that small measurement errors in relative humidity specially in the later stages of the experiment (when remaining volume of pan water is low) cause big changes in $\delta_{E(cal)}$.

The approach to the so-called "steady state value", eq.(4.2), of the pan water is illustrated in Fig.(4.7) for pan 12. The steady state values are shown by the hatched line, relative humidity being 0.82 in this period. It is seen that the pan water strives to approach the steady state value, coming quite close to it around the 27th day of the experiment, and is in good agreement with the observed value until the 35th day. After this, the humidity dropped to 0.72, the weather conditions changed, resulting in a big difference between the observed and the computed steady state values. The sharp, though small, difference observed between the 26th and the 28th day is due to a sudden drop in humidity from 0.82 to 0.78, after which humidity again reached 0.82. The measurements for pan 12 are a bit rough due to the long distance of the site from the weather station, yet the concept of the "steady state values" is quite clear from Fig.(4.7).

4.5 Conclusions

The isotopic fractionation of the evaporating pans is fairly well described by the model. For pans evaporating to dryness it is observed that the optimum initial depth of water should be ≥ 50 mm. This ensures that in the later stages of the experiment, the remaining volume of water is sufficient to effectively damp out atmospheric fluctuations. Whereas constant volume pans are relatively free from this precondition. For the climate in central Sweden, the optimum value of $\beta = 1.016$ is more realistic. The influence of relative humidity on the fractionation is rather large when pan water volumes decrease considerably. However, the predictions of δ_E using equation (3.11) are otherwise quite accurate. It can be concluded that for the climate of central Sweden it is possible to predict quite accurately the fractionation in open water bodies when accurate measurements of relative humidity are available, together with measurements of $\delta^{18}O$ of atmospheric moisture (δ_a) with no strong demands on the accuracy of δ_a . Small fluctuations in δ_a do not affect the δ value of evaporating water considerably. It is also clear

that relative humidity of free atmosphere is enough for the fractionation studies, provided the observations are accurate. Thus, water temperatures need not be recorded and relative humidity normalized to water temperature can be completely dispensed with. This view has also been held by Allison et al. (1979). For the more temperate zones (evaporation being high), it is advisable to check the effect of relative humidity and normalized relative humidity on the computations for the sake of more accurate predictions.

From the isotopic fractionation of pans located in the vicinity of lakes (under investigation), the optimum value of β can be obtained for an accurate determination of δ_E , the lake evaporation. An accurate knowledge of δ_E for various seasons is a must in order to estimate the unknown parameters in the water balance of lakes.

Similarly, for runoff studies with stable isotopes, the magnitude of fractionation in the surface water flow can be estimated from a prior knowledge of pan water fractionation.

5 SOME ASPECTS OF OXYGEN-18 IN PRECIPITATION

5.1 Seasonal effect

Several workers have studied various aspects of stable isotopes in precipitation. Seasonal fluctuations were first observed by Riesenfeld and Chang (1936a,b). They found that, isotopically, winter precipitation is lighter than summer precipitation. To be definite about such a trend it is necessary to investigate a long-term average of all precipitation events on a seasonal basis. It has been very often observed that precipitation differs from event to event depending upon the prehistory of precipitating moisture. Epstein and Sharp (1959), found ^{18}O content of winter snow on glaciers to be lower than summer snow. Similar observations were also reported by Belatini (1959), Sharp and Epstein (1962), Gonfiantini et al. (1963) and Picciotto et al. (1963). Seasonal fluctuations are more predominant in places far away from coastal stations, whereas for locations having maritime climates, seasonal variations are relatively smaller. A world-wide survey of ^{18}O and D in precipitation has been undertaken by IAEA in cooperation with WMO since 1961, and the data are being continuously published by IAEA as Technical Report Series.

5.2 Continental effect

It has been observed that the mean isotopic content of precipitation is generally lower at the inland continental stations compared to coastal stations located at comparable latitudes, Dansgaard (1964). In Western Europe, the depletion rate of heavy isotopes in precipitation as a function of the distance from the coast is lower in summer than in winter and is due to reevaporation of rain in summer. In the Amazon basin, the depletion rate of ^{18}O with regard to distance from the coast is $-0.75 \times 10^{-3}\text{‰/km}$ and is 4 times lower than in Western European precipitation, Salati et al. (1979).

5.3 Latitude effect

The spatial variation of stable isotopes in precipitation is rather interesting from a hydrological point of view. The continental, latitude and altitude (to be discussed next) effects

have been utilised for studying the origin of surface and ground waters. Dansgaard (1964) found that ^{18}O and D concentrations in precipitation were lower at higher latitudes because of the successive rain-outs from the clouds. Each rain-out event causes depletion in the remaining moisture mass and this process is repeated during the moisture transport from the tropics to the poles. The latitude effect for the North American continent is about -0.5‰ per degree of latitude for $\delta^{18}\text{O}$.

5.4 Altitude effect

As regards altitude, various studies, Dansgaard (1953, 1961), Epstein and Sharp (1959), Dinger et al. (1970), Moser and Stichler (1970), and Siegenthaler and Oeschger (1980), have shown that ^{18}O or D content in precipitation decreases with altitude. The $\delta^{18}\text{O}$ lapse rate for altitude for different regions of Europe varies from -0.16 to $-0.4\text{‰}/100\text{ m}$. In Nicaragua, Payne and Yurtsever (1974) found a lapse rate of about $-0.26\text{‰}/100\text{ m}$ for $\delta^{18}\text{O}$. For precipitation in eastern, central and western Himalayas, Bahadur et al. (1977a), obtained a lapse rate $\approx -3.80\text{‰}/100\text{ m}$ for δD . Generally, the altitude and temperature are well correlated in a limited area and the observed depletion with height is purely a multiple condensation effect. At every stage of condensation during the ascent of an air mass over a mountain, the remaining vapour is depleted in its δ value. Consequently the next rain-out from the already depleted vapour will also be depleted relative to the previous condensate (i.e. rain-out).

5.5 Amount effect

For tropical stations, the isotopic content of precipitation is found to be higher in small amounts of rain almost all the year round. This is also the case during peak summer at middle latitudes but never near the poles, Dansgaard (1964). Qualitatively, there are several reasons for this "amount effect". The enrichment of falling raindrops by evaporation during their descent through the relatively dry air below the clouds is considerable for light rains. Superimposed on this is the isotopic exchange between the falling drops and the atmospheric vapour. A clear evidence of enrichment by evaporation from falling raindrops has been reported by Dansgaard (1953, 1961) and by Ehhalt et al. (1963). At higher latitudes (low temperature regions) the amount effect is less pronounced due to smaller

evaporation from the falling raindrops. In the polar regions, the cloud height is low and low temperatures exist which allow very little evaporation and molecular exchange, resulting in almost negligible fractionations in precipitation. Enrichment of falling raindrops is discussed in detail in section 5.12.

5.6 Temperature effect

Assuming that condensation in nature proceeds as Rayleigh's condensation process, it has been possible to correlate the isotopic composition of precipitation with temperature of condensation.

Dansgaard (1953) measured rain from a warm front in which air was moist-adiabatically cooled from 12 to $\approx -8^{\circ}\text{C}$. Interpolating linearly to 12°C , he found that

$$\frac{d\delta^{18}\text{O}}{dT} = 0.45\text{‰}/^{\circ}\text{C}$$

In the lower temperature range (-18 to -30°C), Piciotto et al. (1960) found the following relationship

$$\frac{d\delta^{18}\text{O}}{dT} = 0.9\text{‰}/^{\circ}\text{C} \quad \text{for } ^{18}\text{O} \text{ in Antarctic precipitation.}$$

The latter temperature range is the mean temperature of the cloud sheet at the time of snowfall.

For precipitation samples gathered from different stations representing a wide range of temperature and latitudes, Dansgaard (1961, 1964) correlated the annual weighted mean of ^{18}O in precipitation with annual mean surface temperatures in the following manner:

$$\delta^{18}\text{O} = 0.69 T - 13.6\text{‰}$$

Assuming that the mean surface temperature varies parallel to mean condensation temperature, he found that

$$\frac{d\delta^{18}\text{O}}{dT} \approx 0.7\text{‰}/^{\circ}\text{C}$$

This figure agrees well with the value of $d\delta^{18}\text{O}/dT = 0.66\text{‰}/^{\circ}\text{C}$ in the temperature range -20°C to 5°C after an isobaric cooling. Dansgaard also showed that for all the Greenland icecap

stations ($-30 < T < -10^{\circ}\text{C}$) where the precipitating air masses are moist-adiabatically cooled, $d\delta/dT$ should be equal to $0.67\text{‰}/^{\circ}\text{C}$, which is again in fairly good agreement with the above lapse rate ($0.7\text{‰}/^{\circ}\text{C}$). On the other hand, a lapse rate ($0.521\text{‰}/^{\circ}\text{C}$) for four stations in the northern hemisphere has been reported by Yurtsever and Gat (1981).

Dansgaard further argued that since the observed temperature effects are in agreement with the calculated values, based on the assumption that the water cycle in nature is like a Rayleigh process starting at 20°C , the simplified Rayleigh condensation process suffices for the interpretation of most observations. On the other hand, one cannot as a rule use the isotopic composition of a particular precipitation event as an index of condensation temperature. Each individual event is dependent on several other parameters, namely the thermodynamical conditions during the cooling process, the initial isotopic composition of the moisture, its past history (Kato, 1978, Dansgaard, 1964), and the degree to which reevaporation reenters the precipitating air mass.

5.7 Transport processes of atmospheric moisture and temperature effect in precipitation

As regards the initial composition of atmospheric moisture and its past history, one should regard the trade-wind belts of the oceans as the main source of precipitation. Craig and Gordon (1965) have given a detailed account of the isotopic compositions of surface seawater and precipitation over oceans and continental areas. In the trade-wind belts the sea surface layer is slightly enriched in ^{18}O and D due to high evaporation from the surface. The atmospheric vapour is depleted in ^{18}O relative to seawater by about 10‰ . The first condensate from this vapour will be slightly enriched relative to seawater as condensation occurs at a lower temperature than sea surface temperature (fractionation increases with decreasing temperature). The vapour during its transport poleward gradually loses water by precipitation and since precipitation is always enriched relative to parent vapour the remaining vapour will gradually become depleted polewards.

However, during its passage from trade-wind belts to the poles, water exchange with the sea surface takes place because of rain-outs and evaporation. This exchange varies from place to place and complicates the picture, obscuring any simple relation between the isotopic content of vapour and temperature.

Even for continental areas one has to consider oceans as a source of moisture. The coastal precipitation will not differ much from oceanic precipitation in adjacent areas but as the moisture is transferred inland into the continents it will suffer a depletion in its isotopic content.

A considerable fraction of the precipitated moisture will return to the atmosphere through evapotranspiration with very little change in its isotopic content, as the transpiration part of evapotranspiration is practically nonfractionating; Eriksson (1965) and Zimmermann et al. (1967a). Thus, in continental areas a somewhat simpler relationship between average isotopic content in precipitation and average temperatures can be expected and has been observed as well.

The transport of atmospheric moisture from the trade-wind belts to the poles can be treated in two different manners. The moisture can be transported either as a simple horizontal transport (advective) or as a large-scale eddy diffusion process. The vertical transport is also an eddy-diffusive process although on a different scale; Eriksson (1965). On the other hand, the zonal transport is a mixture between large-scale eddy diffusion and advection. Thus, the temperature effects in precipitation should be discussed in the light of these transport processes separately.

5.8 Horizontal (advective) transport of atmospheric moisture and the temperature effect in precipitation.

In the advective transport of water vapour on a global scale, isobaric cooling by net radiation loss is a possible mechanism for removing water from an air mass. This removal is thought to occur at 850 mbar level, i.e. about 1.5 km a.m.s.l. in the cloud structure.

We now define the term

$$\delta^{\text{‰}} = \frac{R - R_{\text{ST}}}{R_{\text{ST}}} \cdot 1000$$

$$\text{i.e. } 1 + \delta' = \frac{R}{R_{\text{ST}}} \quad \text{where } \delta' = \frac{\delta}{1000}$$

$$\text{then } \frac{dR}{R} = \frac{d\delta'}{1 + \delta'} \quad (5.1)$$

Since we are dealing with the process of precipitation, a recourse to the Rayleigh condensation equation yields (cf. section 3.2)

$$\frac{dR}{R} = (\alpha - 1) \frac{dM}{M} \quad (5.2)$$

where M is the amount of water vapour having an isotope ratio R and condensation removes dM amount of vapour from the original mass M .

Substituting eq.(5.1) in eq.(5.2) we get

$$\frac{d\delta'}{1 + \delta'} = (\alpha - 1) \frac{dM}{M}$$

$$\text{or } d\delta' = (1 + \delta')(\alpha - 1) \frac{dM}{M}$$

$$\text{or } \delta' = (1 + \delta')(\alpha - 1) \ln M \quad (5.3)$$

The temperature derivative of eq.(5.3) yields

$$\frac{d\delta'}{dT} \approx (\alpha - 1) \frac{d}{dT} \ln M \quad (5.4)$$

because δ' is small.

The temperature, T , is expressed in Kelvin. At 850 mbar level where the bulk of precipitation occurs, the amount of vapour or the saturation mixing ratio, M , (in g vapour/kg air) is related to the absolute temperature, T , as

$$\ln M = 21.1 - \frac{5347}{T}$$

in the range $303 > T > 293$ K; Eriksson (1983).

With the temperature derivative the above is written as

$$\frac{d \ln(M)}{dT} = \frac{5347}{T^2} \quad (5.5)$$

Combining eqs (5.4) and (5.5) we get

$$\frac{d\delta'}{dT} \approx (\alpha - 1) \frac{5347}{T^2} \quad (5.6)$$

Equation (5.6) describes the temperature dependence of δ values in precipitation, provided the condensation part of the water cycle in nature is a simple Rayleigh process and further that the vapour is transported by a purely advective process. With the aid of eq.(5.6) one can calculate $d\delta'/dT$ using the mean annual surface air temperatures at a place and compare this slope with the experimentally observed slope for the same place to test the validity of the above expression.

5.9 Eddy transport of atmospheric moisture and the temperature effect in precipitation

As mentioned earlier the poleward transport of water vapour can be considered as a large-scale eddy process; Eriksson (1965). The zonal transport however, is a mixture of large-scale eddy and advection processes. The vertical transport is also an eddy process although on a different scale. From purely statistical considerations, Eriksson (1965) showed that for the exponential gradients of the time averaged humidity of air, M , and the time averaged isotopic composition of atmospheric vapour, R , the following relation holds good for the eddy transport of moisture, i.e.

$$dR/R = (\sqrt{\alpha} - 1) dM/M \quad (5.7)$$

The above expression is similar in form to the Rayleigh condensation formula except that the square root of α (α effective) appears instead of α . Eriksson (1965) also stated that the vertical mixing would probably damp the vertical variations in R .

Consequently, eq.(5.6) can be modified for eddy transport and can be written as

$$\frac{d\delta'}{dT} \approx (\sqrt{\alpha} - 1) \frac{5347}{T^2} \quad (5.8)$$

Equation (5.8) has been used to obtain the theoretical slope ($d\delta'/dT$) using the average surface temperatures for a certain period.

5.10 Temperature effect in precipitation at Uppsala

Precipitation has been collected in the outskirts of Uppsala on a daily basis since July 1981. To avoid evaporation and isotopic exchange between collected water in the rain gauge and

the atmosphere, samples were collected just after the precipitation event. Furthermore, the funnel opening of the rain gauge was also reduced to 3 mm diameter against the normal 8 mm. The location of the rain gauge was about 3 km from the meteorological station of Ultuna. The observations on mean surface temperature, relative humidity etc. were taken from Ultuna. As pointed out earlier, in section 5.1, the single precipitation events should not be used to obtain a direct measure of condensation temperatures; Dansgaard (1961). Therefore, weighted monthly means of precipitation (in $\delta^\circ/\text{‰}$) have been plotted against monthly mean surface temperatures for 1981 to 1984. Since measurements were started in July 1981, a complete annual picture is only valid for 1982 to 1984. However, it is interesting to see and compare the regression line obtained from the daily values of precipitation and surface temperature of rainy days, and the regression line between weighted monthly mean precipitation and monthly mean surface temperatures. Fig.(5.1) shows the regression line between daily precipitation (δ values) and temperature of rainy days for 1983. The regression equation is

$$\delta^{18}\text{O} = 0.351 T - 13.29^\circ/\text{‰} \quad r^2 = 0.392 \text{ (daily) 1983}$$

where T is in $^\circ\text{C}$ and r^2 is the coefficient of variance.

The corresponding regression equation using weighted mean δ of precipitation and monthly mean temperature for 1983 is

$$\delta^{18}\text{O} = 0.378 T - 13.55^\circ/\text{‰} \quad r^2 = 0.906$$

The weighted mean δ s of precipitation and mean temperatures for 1983 are shown in Fig.(5.2).

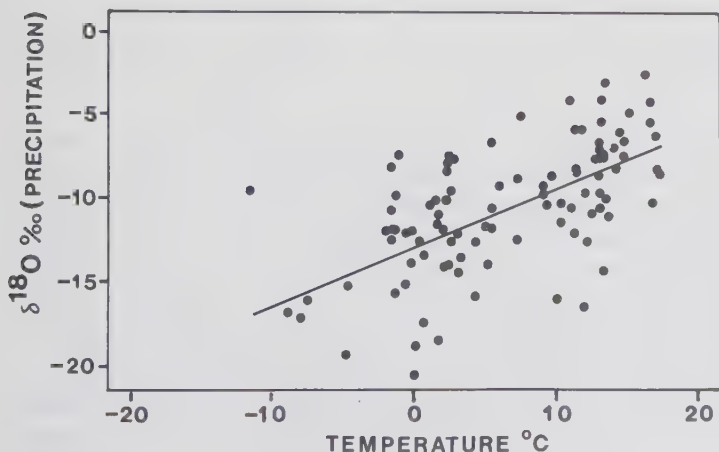


Fig.(5.1) Daily δ values of precipitation versus daily mean air temperatures (ground level) for 1983 at Uppsala.

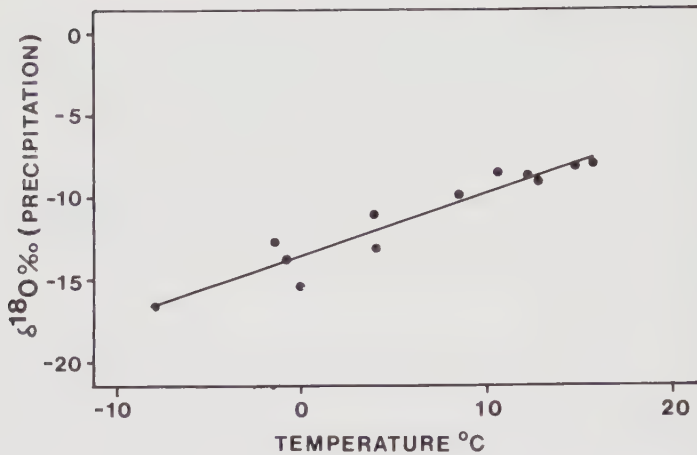


Fig.(5.2) Weighted monthly mean δ values of precipitation versus monthly mean air temperatures (ground level) for 1983 at Uppsala.

It is immediately seen that the correlation coefficient between the daily δ values and temperature is rather low, while it is quite high for weighted mean δ values and monthly mean temperatures. This pattern is also observed for 1981, 1982 and 1984, i.e., the correlation between daily values is poor while it is high for monthly mean values.

Rozanski et al. (1982) observed that the correlation between δD in precipitation and local mean temperatures increases as one moves inland. For Valentia they found $r = 0.78$ but for Stuttgart and Vienna the corresponding values observed by them were 0.89 and 0.96, respectively. The correlation coefficients observed in Uppsala between $\delta^{18}O$ precipitation and local mean temperature vary between 0.91 and 0.95 for 1981 to 1983. Though Uppsala is situated quite near the east coast, the air mass movements are predominantly from west to east. Thus, Uppsala lies sufficiently inland from the west coast to show high correlations. Siegenthaler and Oeschger (1980) correlated the $\delta^{18}O$ in precipitation to climatic parameters, specially temperature, in Switzerland. For Bern (annual mean temperature $8.8^{\circ}C$), they found $d\delta^{18}O/dT = 0.35$ which is quite close to the slopes observed at Uppsala from 1981 to 1984.

The regression equations for 1981-84, using monthly weighted $\delta^{18}\text{O}$ of precipitation and monthly mean temperatures, are

$$\begin{array}{llll} \delta^{18}\text{O} = 0.389 T - 16.25\text{‰} & 1981 \text{ incomplete} & r^2 = 0.876 \\ \delta^{18}\text{O} = 0.477 T - 14.58\text{‰} & 1982 & r^2 = 0.826 \\ \delta^{18}\text{O} = 0.378 T - 13.55\text{‰} & 1983 & r^2 = 0.906 \\ \delta^{18}\text{O} = 0.245 T - 12.77\text{‰} & 1984 & r^2 = 0.4 \end{array}$$

From the above it is concluded that for Uppsala the mean temperature is a good measure of monthly $\delta^{18}\text{O}$ in precipitation. Table (5.1) gives a comparison of the slopes when monthly mean values are considered versus the predicted slopes obtained from eqs.(5.6) and (5.8) assuming advective and eddy transport of atmospheric moisture.

Table (5.1) Observed slopes of the regression line between weighted monthly mean δ value of precipitation versus monthly mean surface air temperature and theoretical slopes from advective and eddy models of atmospheric moisture transport.

Period	Advective model $d\delta/dT = (\alpha-1)5347/T^2 \times 10^3$	Eddy model $d\delta/dT = (\sqrt{\alpha}-1)5347/T^2 \times 10^3$	Observed $d\delta/dT$
(July-Dec)1981	0.723	0.361	0.389
(Jan-Dec)1982	0.742	0.370	0.477
(Jan-Dec)1983	0.735	0.367	0.378
(Jan-Dec)1984	0.730	0.364	0.245
1981-84	0.735	0.367	0.371
Summer 81-84	0.671	0.335	0.371
Winter 81-84	0.810	0.404	0.532

It is seen that the theoretical slopes according to the advective model are almost twice as high as the observed values during all the years as well as during the summer and winter periods. This clearly shows that the advective model of atmospheric moisture transport does not explain the observed relationship between δ values of weighted monthly mean precipitation and monthly mean surface temperatures. Hence, the transport of atmospheric moisture should be treated in a different manner. Kato (1978) found in the Antarctic (freshly fallen snow) that the variations in $\delta^{18}\text{O}$ in precipitation are not only

controlled by temperature of formation but also by the processes responsible for the transport of moisture to the Antarctic ice-sheet, i.e. cyclones. The other possibility is to assume an eddy transport of atmospheric moisture. A fairly good agreement between the observed and theoretical slopes emerges when the eddy model is assumed to hold good; Table (5.1).

The seasonal effect in the $\delta_{\text{precipitation}}$ and temperature relationship is quite obvious from Table (5.1). The months from May to October have been designated as the summer period and the months from November to April are considered as the winter period. The observed slopes for summer and winter periods are 0.371 and 0.532 respectively. The monthly mean temperatures are 12.0°C for the summer period and -0.32°C for the winter period. It is seen that when the mean temperature is low the slope is higher and vice versa. This trend is also verified by the theoretical slopes.

5.11 Oxygen-18 in atmospheric vapour in relation to specific vapour density

As discussed in earlier sections, the relationship between isotopic composition of atmospheric vapour and specific vapour density can be expressed by eqs.(5.2) and (5.7) for the advective and eddy transport of moisture. Replacing M by q (where q is the specific vapour density), and using eq.(5.3) we get the expression for advective transport, i.e.,

$$\delta' = (1 + \delta')(\alpha - 1)\ln q + c \quad (5.9)$$

Similarly in case of eddy transport, α is replaced by $\sqrt{\alpha}$ and we have

$$\delta' = (1 + \delta')(\sqrt{\alpha} - 1)\ln q + c \quad (5.10)$$

It must be borne in mind that q is the average specific vapour density. The atmospheric vapour was collected at a height of 5 m at Uppsala, which is, strictly speaking, hardly a measure of specific vapour density at 850 mbar level. However, as a first approximation, the specific vapour density at 5 m level has been used to calculate the experimental slopes of the regression line between $\delta^{18}\text{O}$ vapour and the natural logarithm of specific vapour density, i.e. $\ln q$. Table (5.2) gives the monthly averages of $\delta^{18}\text{O}$ of atmospheric vapour from July 1981 to December 1984, the monthly mean relative humidity and the monthly mean vapour density which has been calculated from relative humidity and temperature.

Table (5.2) Monthly means of temperature, relative humidity, specific vapour density (q), lnq and $\delta^{18}\text{O}$ of atmospheric vapour; from July 1981 to Dec. 1984

Period	Monthly mean temperature °C	Monthly mean relative humidity %	(q) g/m ³	lnq	Monthly mean $\delta^{18}\text{O}$ vapour ‰
July 81	16.70	77.5	10.52	2.353	-18.68
	14.80	82.5	8.50	2.140	-18.26
	11.40	87.5	9.42	2.242	-19.17
	5.70	92.0	6.72	1.905	-20.00
	0.40	87.5	4.89	1.587	-22.90
Jan. 82	-7.00	88.5	2.81	1.033	-25.84
	-8.60	86.5	2.09	0.737	-23.41
	-4.60	80.5	3.90	1.360	-22.66
	1.30	81.5	4.40	1.481	-20.77
	4.10	64.0	3.49	1.249	-21.60
	9.80	71.5	6.58	1.834	-19.60
	12.60	64.5	6.34	1.846	-20.83
	17.60	69.5	8.37	2.124	-18.73
	16.60	77.5	9.29	2.228	-18.19
	11.50	86.0	8.86	2.181	-17.64
	6.80	91.0	6.95	1.938	-20.06
	4.10	87.0	6.12	1.811	-19.77
	-0.20	90.5	5.22	1.652	-21.80
	0.10	84.5	3.85	1.348	-20.28
	-5.10	84.0	2.27	0.819	-24.15
Jan. 83	-0.70	88.5	4.70	1.547	-22.79
	4.30	82.5	5.44	1.693	-20.78
	10.40	73.5	7.13	1.964	-19.59
	14.50	67.5	7.38	1.998	-18.02
	17.80	67.0	8.57	2.148	-18.53
	17.00	70.0	8.46	2.135	-18.15
	12.00	85.5	8.99	2.196	-19.12
	7.10	81.0	6.92	1.934	-18.84
	0.80	76.5	5.08	1.625	-21.05
	-1.60	85.0	3.70	1.308	-22.78
	-3.70	86.0	3.64	1.291	-23.32
	-2.20	88.0	4.24	1.444	-23.10
	-2.60	78.5	3.37	1.214	-22.97
	5.50	72.0	4.33	1.465	-20.78
	12.00	67.0	7.41	2.002	-19.03
Jan. 84	14.00	74.0	7.96	2.074	-18.64
	15.00	79.0	9.54	2.255	-18.60
	15.70	81.0	10.00	2.302	-19.33
	10.30	91.0	8.57	2.148	-20.22
	8.40	90.5	8.17	2.100	-19.61
	3.10	92.0	5.74	1.747	-21.48
	0.40	87.5	4.93	1.595	-23.56

The regression lines between the observed $\delta^{18}\text{O}$ of atmospheric vapour and $\ln q$ (both quantities on monthly mean basis) are shown in Fig.(5.3) for 1981. The observed and the theoretical slopes for 1981 to 1984 and the coefficient of variance between δ_{vapour} and $\ln q$ are shown in Table (5.3). The theoretical slopes are given for the advective as well as the eddy models of vapour transport. The α in eqs (5.9) and (5.10) is related to the average surface temperatures for the given periods.

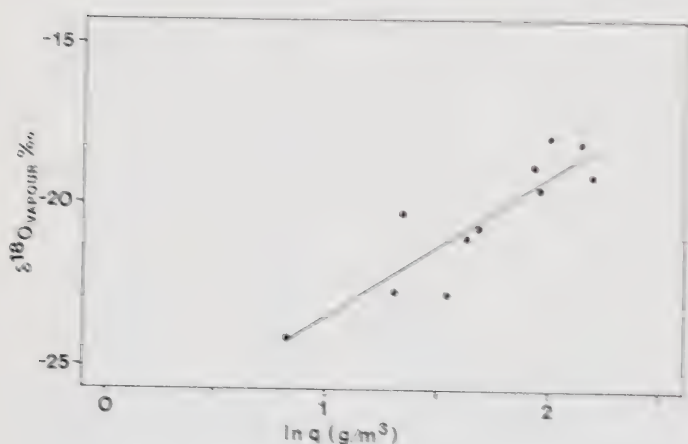


Fig.(5.3) Monthly mean δ values of vapour and $\ln(\text{monthly mean specific vapour density})$, i.e. $\ln q$, for 1981 at Uppsala.

Table (5.3) A comparison of observed slopes of the regression lines between $\delta^{18}\text{O}$ vapour versus $\ln(\text{specific vapour density})$ and the theoretical slopes assuming advective and eddy transport of atmospheric moisture.

Period	Observed slope	(r^2)	Slope advective model	Slope eddy model
(July-Dec) 1981	5.84	0.94	9.8	4.9
(Jan-Dec) 1982	3.70	0.85	10.8	4.9
(Jan-Dec) 1983	4.40	0.81	10.8	4.9
(Jan-Dec) 1984	4.30	0.77	10.8	4.9
(July-Dec) 1981-84	4.23	0.77	10.8	4.9

The correlations between δ_{vapour} and $\ln q$ are quite high. The observed slopes agree quite well with those obtained theoretically from the eddy model, whereas the slopes determined from the advective model are twice as high as those observed. The fairly good agreements found between the slopes of the

regression lines and the slopes obtained from the eddy model in $\delta^{18}\text{O}$ precipitation versus surface temperature and $\delta^{18}\text{O}$ vapour versus $\ln q$ give ample reasons to believe that the transport of atmospheric moisture from the trade-wind belts to the higher latitudes, such as Sweden, has more of an eddy character than purely advection. It is not implied here that the transport is purely eddy in nature, but the role of eddy transport seems to overshadow that of advection.

5.12 Oxygen-18 relationship between precipitation and atmospheric vapour

During the summer season, raindrops that leave the cloud base interact with the surrounding atmosphere, insofar that during their passage through relatively dry air they have sufficient time to evaporate and also exchange with the water vapour. Evaporation will cause enrichment of the raindrops but this process will also continuously change the isotopic composition of the atmosphere between the cloud base and the ground surface on a local basis only. The enrichment of the raindrops has already been referred to in the discussion on amount effect of precipitation.

In a laboratory experiment, Friedman et al. (1962) showed that there is a rapid isotopic exchange between a suspended water droplet and its saturated environment. In their experiment the droplets were kept suspended in an upward stream of saturated air and they experimentally calculated the time required for a raindrop to achieve $1/e$ the isotopic composition of the environment. This time was termed the adjustment time, and the distance travelled during the adjustment time as the adjustment distance. The authors also found that the adjustment time was longer at lower temperatures, e.g. at 30°C and drop size 0.1 cm the adjustment time was about 60 seconds, while for the same size but at 11°C , the adjustment time was 260 seconds.

Generally, raindrops have a radius between 0.01 cm and 0.05 cm, Mason (1975). The corresponding adjustment time and distance for the radii range (0.01 to 0.05 cm) according to Friedman et al. (1962) is thus 7.8 seconds, 5.6 m, and 102 seconds, 410 m, respectively. Hence, according to the size distribution of raindrops, even if they were not created of the same water vapour, they would soon be modified in their isotopic composition. Consequently, the atmosphere will also have an isotopic

picture different from that before the precipitation event. Thus, precipitation will soon reach a near isotopic equilibrium with the atmosphere. Woodcock and Friedman (1963) observed in orographic showers in Hawaii that the deuterium content of raindrops decreased with increasing diameter. They explained that the drops formed at the top of the cloud increase in size during their fall by collecting cloud droplets, while drops formed at the base do not. The drops formed at the (colder) upper part of the cloud will thus be depleted relative to those formed in the (warmer) lower portion. On the other hand, assuming all drops to have the same deuterium content initially, the smaller drops are evaporated faster, getting relatively more enriched. This is specially true for small amounts of rain or in the beginning of a rainstorm.

Facy et al. (1963), in their study of the formation of hailstones by isotopes, assumed isotopic equilibrium between droplets and vapour at all the levels in a cloud system. In laboratory experiments Stewart (1975) found equilibrium fractionation between vapour at the drop's surface and the drop, while kinetic fractionation existed between vapour at the surface of the drop and vapour in the atmosphere. Stewart (1975) found no evidence of kinetic fractionation at the liquid-atmosphere interface during evaporation of falling raindrops. The condensation in clouds has been assumed to be a near-equilibrium process, Dansgaard (1954, 1961) and Rozanski and Sonntag (1982). However, before this equilibrium is achieved the isotopic composition of the lower atmosphere will change slightly until near-equilibrium is finally attained. Craig and Horibe (1967) found the isotopic composition of vapour in continental areas to be in isotopic equilibrium with precipitation. In coastal areas, deviations from equilibrium occur because surface air is already in rough equilibrium with ocean water and not with the rain.

On the other hand, the rapid exchange between water droplets and the atmosphere does not apply to ice crystals and snow flakes or water in any solid form, due to the exceedingly long adjustment time at lower temperatures, Friedman et al. (1962) and Gat and Dansgaard (1972). This is specially true for high latitudes (such as Sweden), particularly in the winter time when most of precipitation occurs as snow.

5.13 Oxygen-18 of atmospheric vapour at Uppsala

Studies on the water balance of lakes and other surface reservoirs using stable isotopes require that the isotopic content of the atmosphere should be known. The δ value of the atmosphere can either be determined experimentally or may be estimated from the precipitation data assuming that precipitation and vapour are in near isotopic equilibrium with each other during the summer months. This further implies that δ values of precipitation and vapour should be well correlated if they are in equilibrium.

Since the δ value of the atmospheric vapour was continuously monitored for purposes explained in section 4, the regression between $\delta_{\text{precipitation}}$ and δ_{vapour} was also studied at Uppsala from 1981 to 1984.

The period from 1982 to 1984 has been divided into summer and winter months. The difference between $\delta^{18}\text{O}$ of precipitation and atmospheric vapour (monthly means) observed at Uppsala and the corresponding difference obtained, assuming isotopic equilibrium at the prevailing temperatures on days having rain or snow, are shown in Table (5.4).

Table (5.4) Weighted monthly mean of $\delta^{18}\text{O}$ of precipitation, monthly mean $\delta^{18}\text{O}$ of vapour, observed δ -difference between precipitation and vapour, theoretical ($\delta_R - \delta_V$) assuming isotopic equilibrium between precipitation and vapour, and monthly mean temperature (on days having rain or snow).

Period	$\delta^{18}\text{O}$ ‰ rain	$\delta^{18}\text{O}$ ‰ vapour	Observed $\delta_{\text{rain}} - \delta_{\text{vap}}$	Eq. value $\delta_R - \delta_V$	Mean temp. °C
Summer 1982	-9.1	-19.3	10.2	10.3	11.34
Summer 1983	-8.8	-18.9	10.1	10.2	12.39
Summer 1984	-9.9	-19.2	9.3	10.2	12.47
Winter 1982	-14.9	-21.1	6.2	16.6	-9.66
Winter 1983	-13.8	-22.0	8.2	~15.0	-2.36
Winter 1984	-12.4	-22.5	10.1	~15.0	0.46

During summers the observed difference between δ_{rain} and δ_{vapour} is about 10‰. The mean temperature during the summers 1982-84 varies from 11.34 to 12.47°C. Assuming that rain and

vapour are in isotopic equilibrium, then their δ -difference should be $\approx 10\text{‰}$. During the summers 1982-83 the observed and theoretical δ -differences agree very well, while the summer period 1984 deviates by $\approx 1\text{‰}$; Table (5.4).

On the other hand, during the winters of 1982 and 1983, there is a big difference between the observed and theoretical equilibrium values, because the equilibrium $\alpha = 1.0152$ at 0°C and 1.0166 at -10°C for solid (ice)-vapour interface, giving the theoretical equilibrium value of $(\delta_{\text{prec}} - \delta_{\text{vap}})$ as 15.2 and 16.6‰ respectively; Gat (1981).

The characteristic of winter 1984 is special. The monthly mean temperature varied from -1.7°C to $+2.3^\circ\text{C}$ and the mean temperature for the whole period was 0.46°C . This implies that during certain periods, fractionation occurred between liquid-vapour phase while in some it was between solid-vapour phase. Hence, it is difficult to ascribe any particular α value to the fractionation process.

The regression line between monthly mean $\delta^{18}\text{O}$ of vapour and weighted monthly mean $\delta^{18}\text{O}$ of precipitation for 1983 is shown in Fig.(5.4). The regression equations for δ_{vapour} and $\delta_{\text{precipitation}}$ for 1981 to 1984 are

$\delta^{18}\text{O}_{\text{vap}} = 0.71 \delta^{18}\text{O}_{\text{prec}} - 11.8\text{‰}$	1981	$r^2 = 0.884$
$\delta^{18}\text{O}_{\text{vap}} = 0.30 \delta^{18}\text{O}_{\text{prec}} - 16.3\text{‰}$	1982	$r^2 = 0.625$
$\delta^{18}\text{O}_{\text{vap}} = 0.69 \delta^{18}\text{O}_{\text{prec}} - 12.7\text{‰}$	1983	$r^2 = 0.673$
$\delta^{18}\text{O}_{\text{vap}} = 0.62 \delta^{18}\text{O}_{\text{prec}} - 14.5\text{‰}$	1984	$r^2 = 0.609$

It may be mentioned that the correlations between δ values of vapour and precipitation are comparatively better than those observed by Schoch-Fischer et al. (1984) in central Europe (0.72 , 0.77 and 0.81 , etc.).

From the above data it is tempting to believe that in summer rain and vapour in the vicinity of ground level are in isotopic equilibrium with each other. Schoch-Fischer et al. (1984) observed at Heidelberg that, during summer, rain and vapour are in isotopic equilibrium. This shows that falling rain drops evaporate and exchange considerably below the cloud layers even in north European climates, though this process was thought to be of consequence in warm and arid climates only.

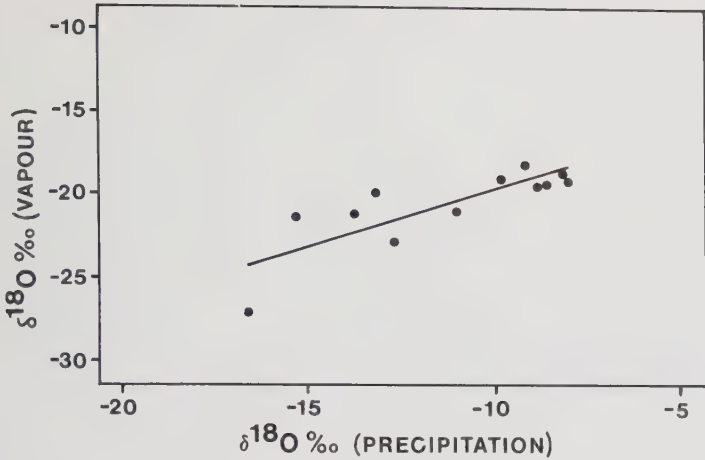


Fig.(5.4) Monthly mean δ values of vapour versus weighted monthly mean δ values of precipitation for 1983 at Uppsala.

Similar conclusions have also been drawn by Rozanski et al. (1982) on the basis of the $\delta\text{D} - \delta^{18}\text{O}$ relationship in summer precipitation in Europe.

On the other hand, during the winter period when the temperature is below 0°C , the difference between precipitation and vapour δ values (considering the snowfall days only) varies from 6 to 10‰ . This difference is small considering that snow-vapour in isotopic equilibrium at 0°C will differ in their δ values by 15‰ and by about 16‰ at -10°C . This shows that vapour and snow are not in isotopic equilibrium with each other. Deviations from equilibrium were also observed by Schoch-Fischer et al. (1984) in Cracow during winters. It is quite likely that snow and the surrounding vapour do not get sufficient time for equilibration as new air masses of varying δ values coming from the Atlantic, and from central and south-eastern Europe keep on changing the isotopic picture of the environment continuously, at least in Uppsala.

Since precipitation and atmospheric vapour are in near isotopic equilibrium during summer, one can roughly estimate the δ value of atmosphere on a weekly or monthly basis for studies regarding the water balance of lakes, etc. It is only during the summer months that the bulk of isotopic exchange between water surface and the atmosphere occurs, while in winter it is of almost no consequence because of the frozen lake surface. Therefore, the inability to estimate δ of atmosphere during winters (because snow and vapour are not in equilibrium) does not pose any problem for lake water balance studies.

5.14 $\delta^{18}\text{O}$ vapour and temperature relationships at Uppsala

Yet another method to check the isotopic equilibrium between precipitation and atmospheric vapour, stems from the precipitation versus temperature and atmospheric vapour versus temperature relationships. If precipitation and vapour are in equilibrium then the difference between the intercepts of the regression equations of $\delta_{\text{precipitation}}$ versus temperature and δ_{vapour} versus temperature should be about 10‰ in summer. The δ values of vapour were studied at Uppsala in relation to local temperature (both on monthly mean basis) as a further test of the precipitation-vapour equilibrium.

At Uppsala the monthly mean $\delta^{18}\text{O}$ vapour values are well correlated to mean local surface temperatures. The use of monthly mean values for vapour and temperature provides a better representation of the prevailing atmospheric circulation pattern over a given region. Correlation between daily values was poor and a large scatter was observed. This was also the case between $\delta_{\text{precipitation}}$ and temperature observed on a daily basis (cf. section 5.10). Below are the regression lines between $\delta^{18}\text{O}_{\text{vapour}}$ and mean surface temperature for 1981 to 1984.

$$\delta^{18}\text{O}_{\text{vap}} = 0.34 T - 23.23\text{‰} \quad r^2 = 0.897 \quad (1981)$$

$$\delta^{18}\text{O}_{\text{vap}} = 0.22 T - 21.61\text{‰} \quad r^2 = 0.797 \quad (1982)$$

$$\delta^{18}\text{O}_{\text{vap}} = 0.25 T - 21.86\text{‰} \quad r^2 = 0.859 \quad (1983)$$

$$\delta^{18}\text{O}_{\text{vap}} = 0.28 T - 22.68\text{‰} \quad r^2 = 0.885 \quad (1984)$$

Fig.(5.5) is a typical example of the regression line between $\delta^{18}\text{O}_{\text{vapour}}$ and temperature.

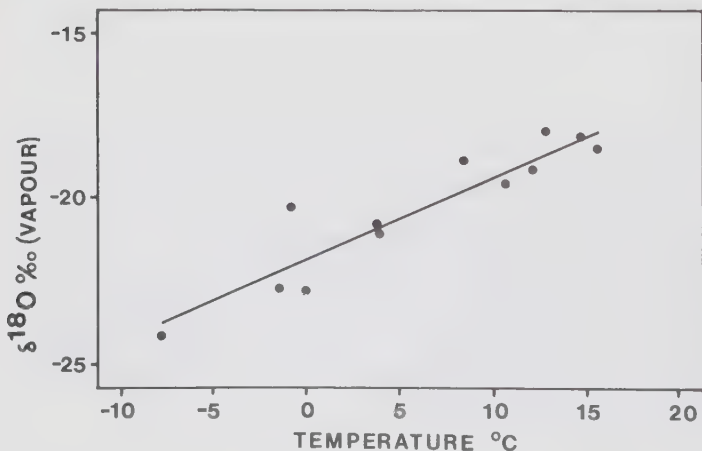


Fig.(5.5) Monthly mean δ values of vapour versus monthly mean air temperature (ground level) for 1983 at Uppsala.

A high correlation was also found by Schoch-Fischer et al. (1984) between δD_{vapour} and mean local temperature, the slope being 3.1 which is in agreement with ^{18}O observations at Uppsala. For ^{18}O in vapour, Schriber et al. (1975) observed a regression equation $\delta^{18}\text{O}_{\text{vap}} = 0.65 T - 12.67\text{‰}$, which is close to Dansgaard's line for precipitation. They attributed this anomaly to errors in moisture sampling. At Uppsala, the intercepts of the regression equations between vapour and temperature are ≈ 7 to 10‰ lower than the corresponding values for precipitation versus temperature (section 5.10), pointing towards equilibrium. Thus, here is yet another proof (though weak) that points towards the near equilibrium condition between precipitation and atmospheric vapour at Uppsala, at least during the summer months.

6 SAMPLING ERRORS IN OXYGEN-18 DUE TO FRACTIONATION IN RAIN GAUGES

6.1 Introduction

Ideally, precipitation samples should be collected from the rain gauges just after a storm event. However, because of the remoteness of the recording stations, it is not always possible to collect samples immediately after the event. Sometimes weekly or twice as frequent the sampling schedule is maintained. Precipitation water, stored in rain gauges, is thus subject to evaporation (though small) and exchange with atmospheric vapour. These processes will bring about a change in the ^{18}O composition depending upon the amount of precipitation, time lag between the storm event and the sampling, design of the rain gauges, ^{18}O content of the atmospheric vapour and the local meteorological conditions. Therefore errors in the δ value of rain due to fractionation during storage in the gauge have to be determined for a reliable data acquisition.

The following pilot study was undertaken to assess the extent of ^{18}O fractionation in precipitation water stored in standard SMHI (Swedish Meteorological Hydrological Institute) type rain gauges. The experiment was conducted during autumn 1980.

Consider that V is the volume of rain water in a rain gauge with A as the surface area. Without taking into consideration the physical processes of isotopic exchange, the rate of change of $\delta^{18}\text{O}$ of the stored water as a first approximation can be expressed as

$$\frac{d\delta}{dt} = K' \cdot \frac{A}{V} = \frac{K'}{d} \quad (6.1)$$

where K' ($\text{LT}^{-1}\text{‰}$) is a constant of proportionality and d is the depth of water.

By measuring $d\delta/dt$ of the stored water, K' can be determined for a certain volume and area of water under constant weather conditions. The factor K' will thus give a measure of fractionation as a function of stored water volume or depth.

Evaporation from a rain gauge is aptly described by eq.(3.15), and it is obvious that eq.(6.1) is a crude approximation. Since

the δ values of atmospheric vapour, relative humidity and temperature, etc. were not recorded in this study, recourse had to be taken to eq.(6.1).

6.2 Experimental set-up

The experiment was carried out in a garden in central Uppsala. The site is 4 km from Ultuna meteorological station, wherefrom data have been used for this site. Five SMHI-type rain gauges were installed in a grassy field at a height of 1.5 m above ground level, with sloping plexiglass shields at the top, and a clearing of 20 cm from the upper edges of the rain gauges. SMHI gauges have a surface area (internal) of 200 cm², which means that 1 mm of precipitation amounts to 20 ml in volume. Two replicates, simulating a precipitation of 10 mm (200 ml) and 30 mm (600 ml) were alternatively placed and the fifth gauge (empty) was used as a control to monitor the effectiveness of plexiglass shields in preventing entry of rain. Gauges no. 1 and 2 had 10 mm, and no. 3 and 4 had 30 mm of simulated rain water. This water was taken from a nearby stream, having a δ value (-10.8‰) close to that of precipitation during that time of year. 5 ml water was removed periodically from each gauge and analysed for ¹⁸O in a ratio type mass-spectrometer. The experiment continued for 32 days, after which a severe rainstorm forced the experiment to be abandoned as some rain water was found to have entered the control rain gauge.

It was later discovered that rain gauges no. 1, 3 and 4 were exactly alike while gauge no. 2 had a raised bottom. Hence, for the sake of comparison, data from gauges no. 1, 3 and 4 are considered.

6.3 Results and discussions

For gauges no. 1, 3 and 4, the values of $\delta^{18}\text{O}$ versus time are plotted in Fig.(6.1). The measurement period can be divided into 3 subperiods in terms of graphic representation, i.e. from 9-19 Sept., 19-26 Sept. and 26 Sept.-10 Oct. For gauges 3 and 4 the rate of enrichment is almost the same for the whole period. The middle period has a smaller slope, i.e. the rate of enrichment was lower. This smaller rate of enrichment during the middle period is due to relatively lower evaporation. Some meteorological parameters are plotted in Fig.(6.2). During the 1st and the 3rd period, potential evapotranspiration was much higher than in the 2nd period, consequently fractionation was

also higher during these periods. Unfortunately data on $\delta^{18}\text{O}$ of atmospheric moisture are missing; hence a purely theoretical simulation of gauge water $\delta^{18}\text{O}$ is difficult. For the sake of simplicity, one can regard potential evapotranspiration as a rough index of evaporation from the gauges, which is further an index of the amount of enrichment of the gauge water.

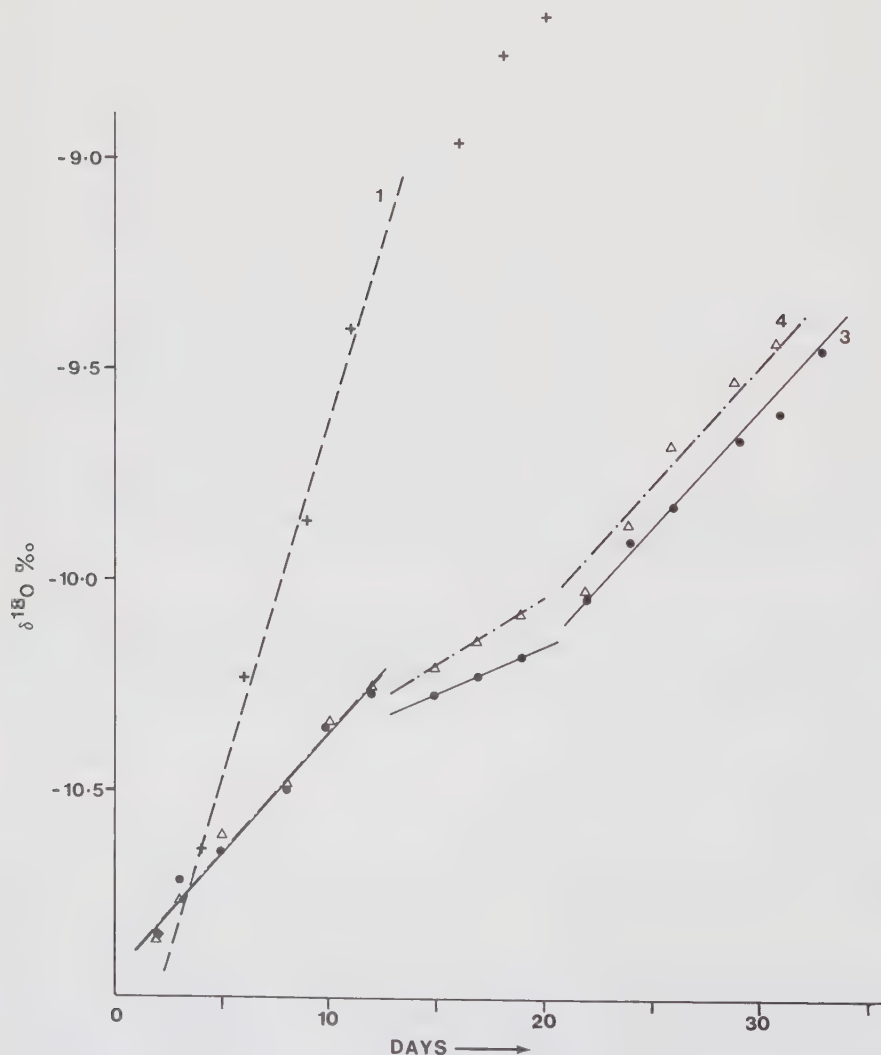


Fig.(6.1) Observed fractionation of ^{18}O in rainwater in rain gauges after the rain storm. Gauge 1 = 10 mm, gauges 3 and 4 = 30 mm of simulated rain. Beginning of experiment 9 Sept. 1980.

The slope of gauge no. 1, Fig.(6.1), is roughly thrice as high as those of no. 3 and 4, which agrees with the ratio of volumes (1:3). The factor K' , 0.14, 0.16, 0.16‰/mm/day (for the initial stages) for gauges 1, 3 and 4, respectively, is quite similar for all the three gauges.

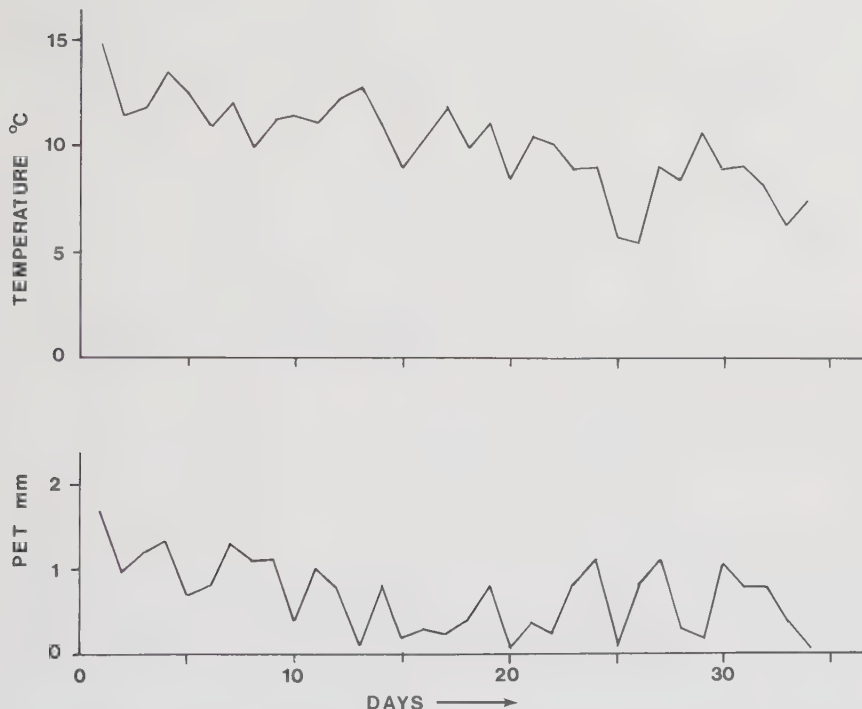


Fig.(6.2) Daily mean temperature and potential evapotranspiration at Uppsala.

6.4 Conclusions

It is clearly evident that there is a definite and considerable enrichment in rain water prior to its collection. The enrichment is in direct proportion to available volume (i.e. depth), implying that smaller amounts of precipitation are prone to higher enrichments and consequently have higher uncertainties in their measured ^{18}O concentrations.

From the present experiment it is seen that during autumn the enrichment in a 10 mm rain event is about 0.2‰/day or about 1.4‰/week, while for a 30 mm rain event the corresponding enrichment would be about 0.06‰/day or about 0.4‰/week.

One can expect still greater rates of enrichment during summer periods when evaporation is high. There is a need to be aware of such variations when immediate sampling or collection of rain water is not possible. It may also be possible to apply corrections to a sample, provided the "rest-time" in the gauge is known. The best alternative is of course to avoid evaporation and mass exchange as far as possible. Adar et al. (1980) developed a self-sealing rain sampler to avoid fractionation of rain water in the gauges, in the Sinai desert in Israel.

7 OXYGEN-18 FRACTIONATION IN INTERCEPTION AND THROUGHFALL

7.1 Introduction

Before precipitation reaches the soil surface, part of it is intercepted by the tree canopy. The incoming raindrops continue to "fill up" the leaves until this canopy reservoir is filled to its maximum capacity and then dripping begins. However, wind action hastens the process of dripping and dripping may begin even when the canopy reservoir has not reached its maximum capacity. That part of rain which goes straight through the open spaces between leaves plus the water that drips down is termed as throughfall. Conceptually, rainfall and throughfall in one storm event have been described by Rutter et al. (1971) and Bringfelt and Hårsmar (1974) in the following manner:

If rainfall R does not exceed a certain amount R_0 , then throughfall T is a function of R such that

$$T = C \cdot R \quad (7.1)$$

where C is the fraction of rain which falls through the canopy without striking any surface and corresponds to that proportion of open space which can be seen through the canopy. C is also called the free throughfall coefficient. If $R \geq R_0$ then the canopy gets saturated and water drains or drips from the canopy during and after the rain storm. The amount of water (say S) that can be stored by the canopy is analogous to the storage capacity of Zinke (1967) or the canopy saturation value of Leyton et al. (1967).

$$\text{When } R \geq R_0, \quad T = R - S - E \quad (7.2)$$

$$\text{and } S = (1 - C)R_0 \quad (7.3)$$

where E is the evaporation from the canopy reservoir and S is the canopy reservoir or storage capacity. R_0 is the critical amount of rain required to fill the canopy reservoir. In the present case, stemflow is assumed to be negligible for trees with downward sloping branches. Delfs (1965) found stemflow to be about 1% of rainfall in Norway spruce.

Intercepted water is subject to evaporation and part of it drips down while the rest of it is evaporated back to the atmosphere. The fraction of rainfall which never reaches the

ground and is evaporated is called interception loss. During the time rainwater is held by the canopy, it is subjected to evaporation and isotopic exchange with the atmospheric moisture. The processes of evaporation and isotopic exchange bring about a change in the isotopic composition of intercepted water. Generally, these processes cause isotopic enrichment of the intercepted water but in some cases depletion may also occur. The enrichment or depletion of intercepted water are dictated by several factors, namely the relative humidity, the difference between δ values of rain and atmospheric moisture ($\delta_p - \delta_a$) and the temperature of fractionation. It is obvious that the intercepted water will strive to reach an isotopic equilibrium with the atmosphere, resulting either in enrichment or depletion depending upon the above-mentioned factors. Hence, the net rain water or throughfall reaching the soil surface, consisting of direct rainfall and dripping of the canopy water will not have the same isotopic composition as that of the original rain. Knowledge about the isotopic composition of throughfall is important for studies concerning the use of isotopic composition of meteoric waters as hydrological tracers, to investigate the origin of groundwaters. This has also been stressed by Gat and Tzur (1967). The isotopic fractionation of throughfall can have far-reaching consequences for warm climates where the amount of fractionations can be considerable. In the streamflow separation studies, using stable isotopes, estimates of the contributions of surface runoff and groundwater to streamflow are influenced by the rain input and its isotopic composition. In a basin where the areal extent of the tree canopy is significant, an accurate knowledge of the throughfall and its isotopic composition is very important.

7.2 Isotopic fractionation in throughfall - some theoretical aspects

In a continuous rain, when the canopy reservoir capacity is exceeded, the throughfall, T , can be expressed as

$$T = T_C + T_F - E \quad (7.4)$$

where T_C is the overflow from the canopy, T_F is the fraction of rain coming as free throughfall and E is the evaporation from the canopy. Further

$$T_C = R(1 - C) \text{ and } T_F = R \cdot C$$

where C is the free throughfall coefficient.

The isotopic content of the throughfall (δ_T) is

$$\delta_T = (\delta_c \cdot T_C + \delta_p \cdot T_F) / T \quad (7.5)$$

where δ_c and δ_p are the δ values of the canopy reservoir and rain respectively.

For the calculation of δ_c , it must be borne in mind that the canopy reservoir is subjected to fractionation as soon as it begins to fill, and after saturation is reached further rain inputs generate overflow. Thus we have a system of open water body with inputs as rain and outputs in the form of evaporation and overflow. For the sake of simplicity, this system is assumed to be isotopically well mixed.

Equation (3.26) gives the time rate of change of the δ value of the canopy reservoir, and in terms of the new variables can be written as

$$\frac{d\delta_c}{dt} = \frac{E(\delta_c - \delta_E) - I(\delta_c - \delta_p) + Q(\delta_c - \delta_Q)}{S_0 - \int_0^t (E + Q - I) dt} \quad (7.6)$$

For the present case, S = amount of water in the canopy reservoir, I = rain on canopy, Q = overflow from the canopy and E = evaporation and δ_c , δ_p , δ_E and δ_Q are the δ values of the canopy reservoir, rain, atmospheric vapour and overflow from the canopy, respectively. A mathematical model has been worked out to compute δ_c .

For rains exceeding R_0 , $E + Q - I = 0$ and $\delta_c = \delta_Q$ in eq.(7.6) and its new form is

$$\frac{d\delta_c}{dt} = \frac{E(\delta_c - \delta_E) - I(\delta_c - \delta_p)}{S_0} \quad (7.7)$$

S_0 in the above case is kept constant, which is the observed canopy reservoir capacity. From the above equations, knowing the values δ_p , δ_E , E and I , time rate of changes in δ_c can be calculated.

The δ value of the evaporate, i.e. δ_E , can be obtained from eq.(3.11), which for the present case is written as

$$\delta_E = \frac{1/\alpha(1+\delta_c) - h(1+\delta_a)}{(1-h)\beta} - 1 \quad (7.8)$$

δ_a being the δ value of atmospheric vapour, h the relative humidity, α the fractionation coefficient and β a constant.

Initially, the δ value of the canopy will be the same as the δ value of rain, i.e., $\delta_c = \delta_p$. Due to evaporation and molecular exchange with the atmospheric vapour, the canopy water will tend to achieve an isotopic steady state or equilibrium with the atmosphere. The δ value of the canopy reservoir at steady state is given by δ_{cs} , such that

$$\delta_{cs} - \delta_a = (1 + \delta_a) \frac{\frac{1}{\alpha} - h - \beta(1-h)}{\beta(1-h) - \frac{1}{\alpha}} \quad (7.9)$$

In the present case it is just an approximation of the true δ_{cs} , because neither further mixing of the canopy water with incoming raindrops nor canopy overflow is considered. Thus, δ_{cs} and δ_p are synonyms here.

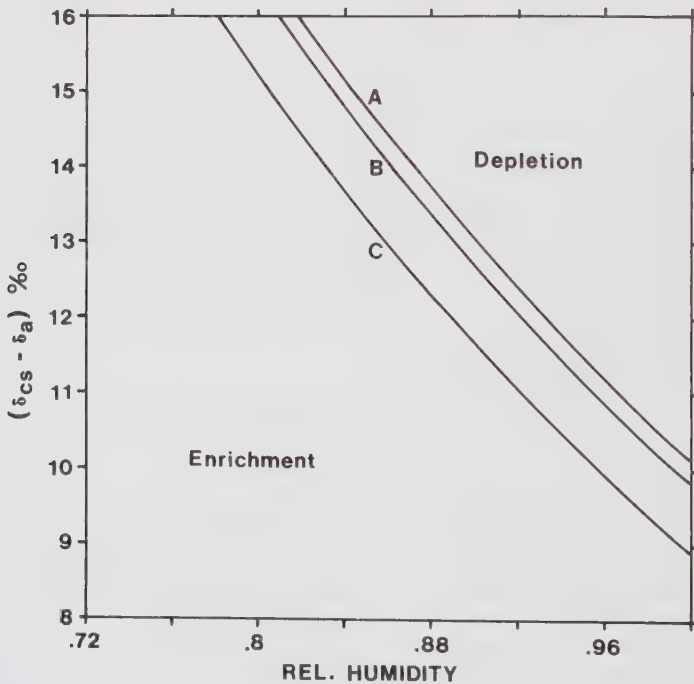


Fig.(7.1) The isotopic difference between the "steady state value" (δ_{cs}) of canopy water (synonymous with rain δ_p) and atmospheric vapour versus relative humidity. $\alpha = 1.0103$ (10°C), 1.010 and 1.0090, for curves A, B and C respectively.

The variation of $\delta_p - \delta_a$ with respect to humidity is shown in Fig.(7.1), wherefrom, knowing the prevailing relative humidity during the rainfall, one can qualitatively predict whether the throughfall will be enriched or depleted with respect to a certain rainfall. For example, if temperature during rainfall is 10°C, then $\alpha = 1.0103$ and curve A is valid. Assuming that $h = 0.97$, then for $\delta_p - \delta_a \leq 10.95\text{‰}$ enrichment will take place, while $\delta_p - \delta_a \geq 10.95\text{‰}$ will cause depletion, and for $\delta_p - \delta_a = 10.95\text{‰}$ equilibrium is attained.

Using eqs (7.5, 7.7, and 7.8) a mathematical model has been worked out to simulate δ_T . S_0 is given a start value 0.1 mm and $\delta_c = \delta_p$ for the first step of evaporation. Experimentally observed values of $S = 2$ mm, $R_0 = 4$ mm and $C = 0.5$ (explained later in the text) were used in the model calculations. Simulations of δ_T were done only for those events for which rainfall exceeded 4 mm. For events ≤ 4 mm, the canopy reservoir does not saturate, there is no dripping from the canopy and ideally δ_T should be equal to δ_p .

7.3 Field studies of interception and ^{18}O fractionation in throughfall

To determine what fraction of rainfall is intercepted by the tree canopy and to assess the overall fractionation occurring in throughfall, field studies were initiated at Studsvik in 1981 and at Uppsala in 1983.

Preliminary studies on the ^{18}O fractionation in throughfall were started at Studsvik. The canopy consisted of young *Salix smithiana* trees. Precipitation was collected above the tree canopy while throughfall was collected in 4 gutters near the ground surface below the trees, on a daily basis. $\delta^{18}\text{O}$ of atmospheric vapour and relative humidity observations are not available for Studsvik.

A more serious attempt to determine interception loss and fractionation in throughfall was made in Uppsala during July-September 1983 in a dense pine forest. Precipitation was collected in an open area about 15 m from the edge of the forest. Using a tipping-bucket type rain gauge, throughfall was collected in the forest in 4 gutters, each 5 m long. The total area of the gutters was $(4 \times 5 \times 0.1 \text{ m}^2)$, i.e. 2 m^2 . All four gutters emptied into a 25 litre can placed below the ground surface. Rainfall as well as throughfall were collected not more than 5 hours after the event. $\delta^{18}\text{O}$ of atmospheric vapour

was monitored about 5 km away from the forest, on a daily basis. From the tipping-bucket rain gauge, the intensity of rainfall, the duration of rainfall, and the dry periods between successive rainfall events were also measured.

A throughfall exceeding 12.5 mm resulted in overflow of the can. Hence, only the observations for throughfall ≤ 12.5 mm have been considered for interception losses.

7.4 Results and discussions

7.4.1 Canopy reservoir capacity and rainfall-throughfall relationships

Rain and throughfall of 24 storm events, Table (7.1), observed at Uppsala from June to September 1983, are shown in Fig.(7.2). For rains ≤ 3.7 mm the data points are evenly distributed along

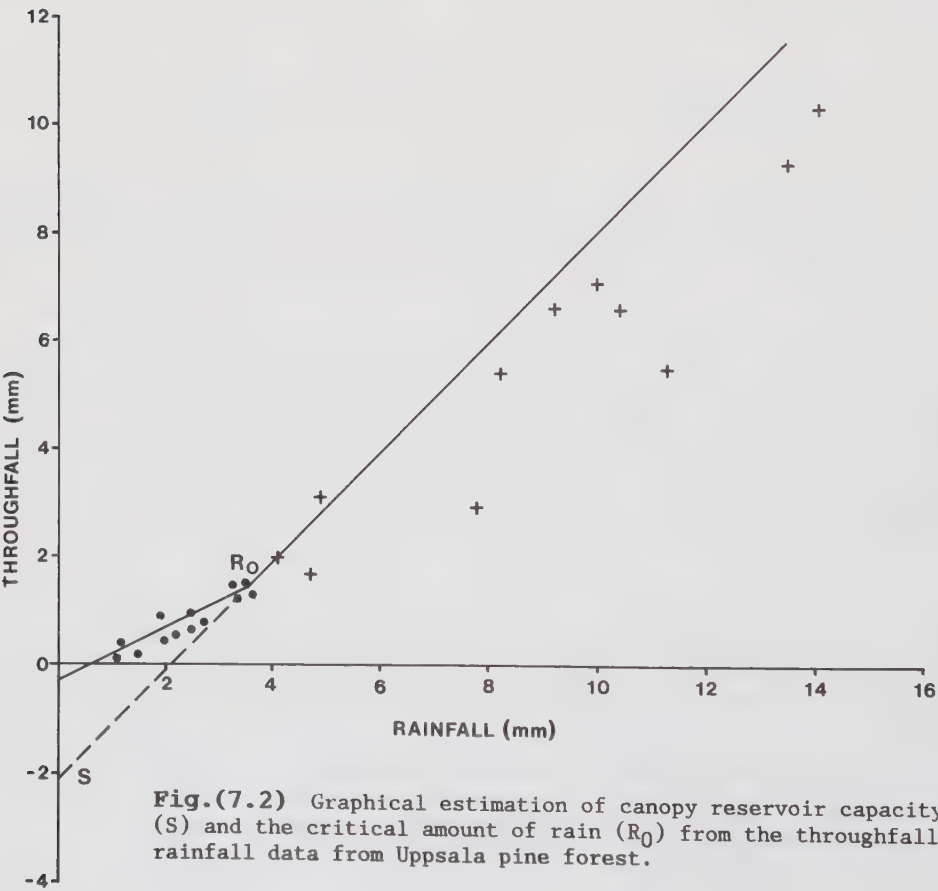


Fig.(7.2) Graphical estimation of canopy reservoir capacity (S) and the critical amount of rain (R_0) from the throughfall rainfall data from Uppsala pine forest.

Table (7.1) Amount and $\delta^{18}\text{O}$ of rain and throughfall, isotopic difference between rain and atmospheric vapour ($\delta_p - \delta_a$), throughfall and rain ($\delta_T - \delta_p$), predicted enrichment/depletion from Fig.(7.1) in throughfall and simulated δ value of throughfall (δ_T) from the model, for the pine forest at Uppsala.

Date	Rainfall (mm)	$\delta^{18}\text{O}$ rain (‰)	Through- fall (mm)	$\delta^{18}\text{O}$ through- fall (‰)	($\delta_p - \delta_a$) (‰)	($\delta_T - \delta_p$) (‰)	Predicted enrichment /depletion	Simulated δ_T (‰)
83-06-02	10.0	-5.4	7.1	-5.2	11.4	0.3	D	-5.2
83-06-04	1.1	-8.2	0.1	-8.3	11.0	-0.1		
83-06-05	14.0	-9.6	10.3	-9.1	9.5	0.5	E	-9.1
83-06-27	2.5	-4.7	0.6	-4.8	13.9	-0.1		
83-06-28	3.6	-8.0	1.3	-7.4	10.6	0.6		
83-06-29	13.5	-15.6	9.2	-15.3	3.8	0.3	E	-15.4
83-06-30	7.8	-10.0	2.9	-9.7	9.4	0.3	E	-9.5
83-07-01	4.9	-9.1	3.1	-8.9	8.8	0.2	E	-8.7
83-07-02	1.9	-7.6	0.9	-7.1	10.2	0.5		
83-07-04	2.0	-6.2	0.4	-6.4	13.9	-0.2		
83-07-04	1.5	-10.4	0.2	-10.2	9.7	0.2		
83-07-18	1.0	-5.4	0.2	-5.4	14.9	0.0		
83-07-28	3.5	-6.5	1.5	-6.4	10.8	0.1		
83-07-28	9.2	-8.6	6.6	-8.3	8.7	0.3	E	-8.3
83-07-30	3.3	-8.7	1.5	-8.7	10.6	0.0		
83-08-12	10.5	-11.3	6.6	-11.0	9.0	0.3	E	-10.0
83-08-24	2.2	-8.5	0.5	-8.3	11.2	0.2		
83-08-27	1.2	-4.8	0.4	-4.8	12.9	0.0		
83-09-04	2.5	-6.3	0.9	-6.7	11.1	-0.4		
83-09-08	4.7	-16.4	1.7	-15.6	6.4	0.8	E	-14.4
83-09-16	11.3	-8.7	5.4	-8.2	9.6	0.5	E	-8.1
83-09-21	3.3	-9.0	1.2	-9.0	10.5	0.0		
83-09-23	8.2	-9.3	5.4	-8.6	10.3	0.7	E	-8.7
83-09-24	17.2	-9.9	10.4	-8.7	10.2	1.2	E	-9.0

a line, but for rain amount ≥ 3.7 mm, the upper envelope of the observation points steepens and the values of throughfall for given values of rainfall get rather scattered. The inflexion point, R_0 , of the upper envelope represents the canopy saturation, Rutter et al. (1971), which in the present case is 3.7 mm. Thus, for the critical rain amount (R_0) = 3.7 mm, the canopy reservoir is completely filled and further rain drips from the canopy as overflow, such that throughfall $T = R - E$. To the left of the inflexion point, i.e. for rain ≤ 3.7 mm, throughfall can be expressed as

$$T = C \cdot R$$

The regression line between throughfall and rain for $R \leq 3.7$ mm is

$$T = 0.49 R - 0.3 \quad (r^2) = 0.85$$

(Ideally, there should be no intercept.)

Thus the experimental value of C , the free throughfall coefficient for the Uppsala pine forest, is about 0.5.

For $R \geq 3.7$ mm the regression equation is

$$T = 0.72 R - 1.06 \quad (r^2) = 0.87$$

The observed slope of the upper envelope is close to 1, Fig.(7.2), which agrees with the ideal slope = 1, since after the canopy saturation $T = R - E$, E the evaporation being negligibly small during the rain fall. Generally, the value of E during the rain is assumed to be ≈ 0.1 mm/h. It is assumed that the vertical scatter of the points to the right of the inflexion point is mainly due to variation in evaporation from the wet canopy, Leyton et al. (1971). The negative intercept of the upper envelope on the throughfall axis is the canopy reservoir capacity and is about 2.1 mm at Uppsala. The critical value of rain, R_0 , may now be calculated from eqn (7.3), since S and C are already known. From eq.(7.3), $R_0 \hat{=} 4.1$ mm which agrees fairly well with the graphical estimation of $R_0 = 3.7$ mm obtained earlier. For a coniferous forest in the Velen basin, Sweden, Bringfelt and Hårsmar (1974) obtained $S = 2$ mm, $C = 0.5$ and $R_0 = 4$ mm. It is seen that a similar picture emerges for the pine forest in Uppsala too. The interception loss at Uppsala, for $R \geq 4$ mm is about 42% of rainfall and for all the storms is $\approx 44\%$ compared to 20% total loss obtained by Bringfelt and Hårsmar (1974), 20 to 40% for coniferous forests obtained

by Zinke (1967) and 36% in old Norway spruce obtained by Delfs (1965). On the other hand, Rutter et al. (1971) found S to vary from 1 to 1.3 mm, $C \approx 0.25$ and the interception loss varied from 12 to 42% in individual storms in Corsican pines.

At Studsvik, rainfall in only one event, Table (7.2), is less than 4 mm and the data are insufficient for estimation of C . Only a very rough estimate of S can be obtained which is about 2 mm, Fig.(7.3). The interception loss at Studsvik is $\approx 50\%$ of the rainfall.

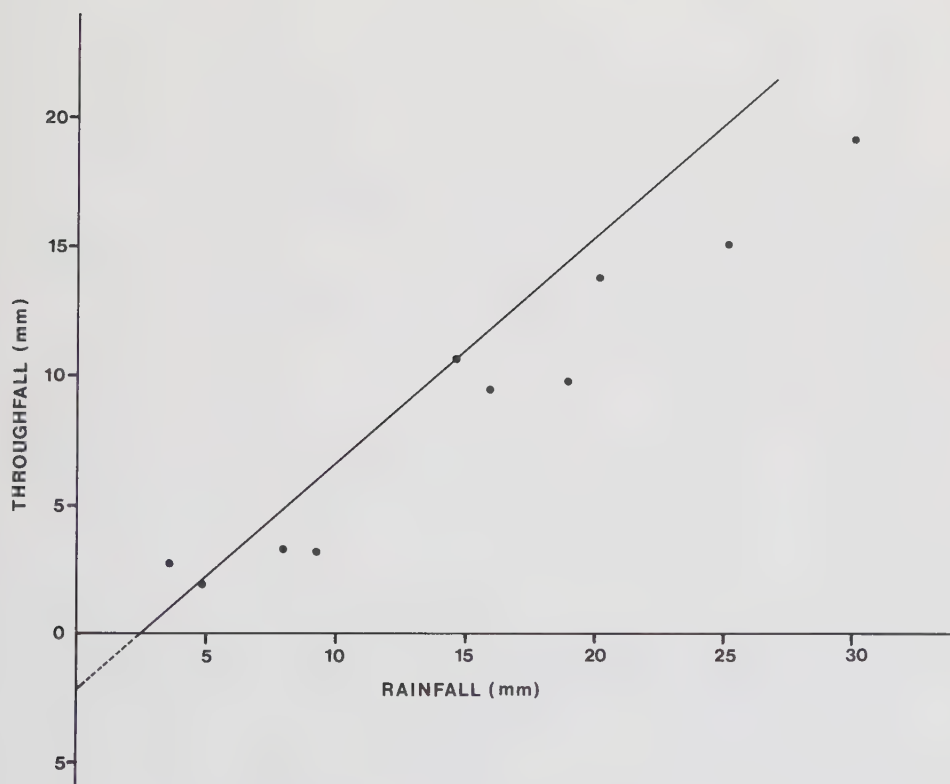


Fig.(7.3) Throughfall and rainfall relationship at Studsvik (Salix trees).

Table (7.2) Amount and $\delta^{18}\text{O}$ of precipitation (rain) and throughfall at Studsvik. The predicted enrichment or depletion in throughfall from Fig.(7.1) are also shown as well as the percentage loss by interception. D* indicates observed depletion against predicted enrichment in δ_T .

Date	Precipitation (mm)	$\delta^{18}\text{O}$ precipitation δ_p ‰	Throughfall (mm)	$\delta^{18}\text{O}$ throughfall δ_T ‰	$(\delta_T - \delta_p)$ ‰	Predicted enrichment/depletion	Interception % of rain
1981-07-23	-	-9.0	-	-8.0	1.0		
1981-07-29	7.9	-8.6	3.2	-8.4	0.2	E	59.5
1981-08-06	9.2	-8.4	3.2	-8.1	0.3	E	65.2
1981-08-12	20.2	-8.1	13.9	-7.7	0.4	E	31.2
1981-08-18	25.3	-10.6	15.2	-11.7	-1.1	E D*	39.9
1981-08-26	18.9	-12.5	9.8	-12.0	0.5	E	48.2
1981-09-11	3.5	-8.8	2.8	-11.8	-3.0	E D*	20.0
1981-09-23	14.5	-11.1	10.7	-10.9	0.2	E	26.2
1981-09-30	4.7	-8.4	1.9	-9.2	-0.8	E D*	59.5
1981-10-07	15.8	-9.5	9.5	-8.5	1.0	E	39.8
1981-10-21	30.3	-14.0	19.3	-12.7	1.3	E	36.3

7.4.2 Fractionation in throughfall

The isotopic differences ($\delta_p - \delta_a$) between rain and atmospheric vapour for the rain events ≥ 4 mm have been checked qualitatively using Fig.(7.1), curve A. It has been found, Table (7.1), that barring 1 event out of 11, all the events at Uppsala show enrichment as predicted by the trend curve A. This shows that qualitatively the trend curve A is a good measure of the nature of fractionation occurring in the canopy reservoir. Alternatively, the isotopic difference ($\delta_T - \delta_p$) between throughfall and rainfall has been plotted against ($\delta_p - \delta_a$), Fig.(7.4).

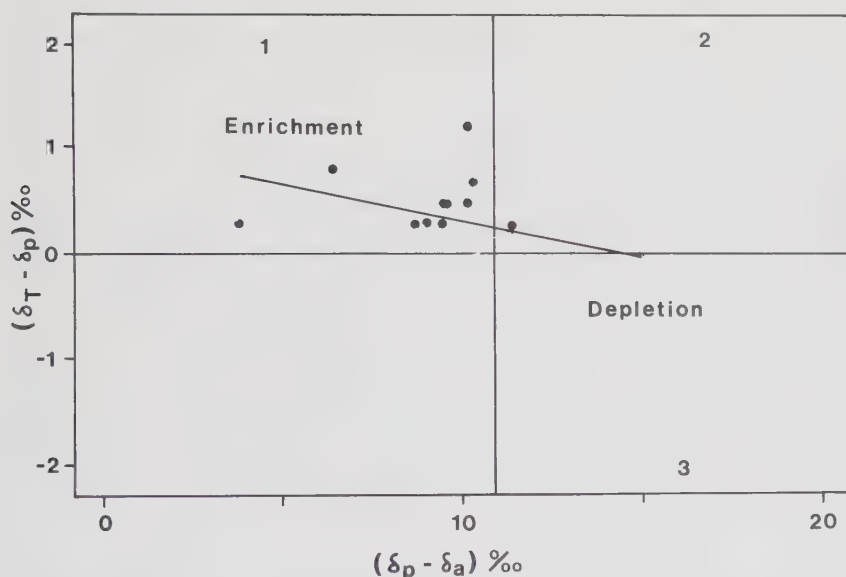


Fig.(7.4) Qualitative representation of fractionation in throughfall. δ_T , δ_p and δ_a are the δ values of throughfall, rain and atmospheric vapour, respectively.

Since isotopic equilibrium between canopy water and atmosphere is attained when $(\delta_p - \delta_a) = 10.95 \text{‰}$, block 1 shows enrichment and block 3 depletion. It is seen graphically that only 1 event, block 2, having $\delta_p - \delta_a > 10.95 \text{‰}$ shows enrichment, whereas according to prediction from curve A it should be depleted. The single disagreement observed depends upon a variety of other processes which can completely change the isotopic picture of the throughfall.

Dansgaard (1953) observed that a single rain may or may not be uniform in its ^{18}O content as rain proceeds with respect to time. For example, in showers the ^{18}O of rain decreased somewhat at the end, while in a warm-front, the initial rain had low ^{18}O while the later part was increasingly heavy. Ehrlert et al. (1963) and Matsuo and Friedman (1967) also reported that deuterium content in rain varied with time. Rainwater was enriched in the beginning and got depleted in the end. The increase in heavy isotope was markedly high when rain intensity was low and became fairly uniform at high intensities. Assuming that rain is isotopically lighter at the end, then part of the end portion will be held in the tree canopy and the throughfall will be enriched. On the other hand, if rain is lighter in the beginning, then the throughfall will be depleted. In the light of the above circumstances, we are faced with a complex interplay between fractionation in the canopy and the differential isotopic content of single rain storms. Thus, in the present discussions, we assume that in general the rainfall is more or less uniform in its ^{18}O content. Simulations have been made to estimate δ_T , i.e. the δ value of throughfall. Simulations have been done only for events exceeding 4 mm, the critical amount of rain. The evaporation during the rain has been assumed to be 0.1 mm/h, relative humidity (h) has been varied from 90 to 96% and the temperature has been kept constant, i.e. 10°C. The isotopic content of atmospheric vapour, δ_a , is equal to the values observed on the rainy days. It is observed that the observed and simulated δ values of throughfall in Table (7.1) agree fairly well. The regression equation between δ_T simulated and δ_T observed for 11 events is

$$\delta_T(\text{sim}) = 0.93 \delta_T(\text{obs}) - 0.42\text{‰}.$$

The coefficient of variance $r^2 = 0.98$. δ_E is very sensitive to small variations in (h) and so is δ_C . Thus a small change in h results in a sharp change in δ_T . The simulations therefore have an inherent drawback on account of the uncertainty in the measurement of (h). During the experiment, (h) was not measured in the field, therefore only expected values of (h) have been used in the simulations. At Studsvik, fractionation in throughfall has been qualitatively checked from Fig.(7.1), using the δ_a values monitored at Uppsala in 1981. It is seen from Table (7.2) that three events out of eleven do not agree with the predictions from Fig.(7.1). These events at Studsvik show rather enormous depletions ranging from -1 to -3‰; Table (7.2). On the other hand, the highest depletion observed at Uppsala is -0.4‰. A depletion of -3‰ hardly seems possible

by isotope exchange only. Perhaps the storms had a variable distribution of ^{18}O , being light in the beginning and getting progressively heavier in the end. One is forced to make such speculations when the ^{18}O distribution in rain with respect to time is not known.

From the weighted mean isotopic content of rain and throughfall at Uppsala it is found that throughfall is enriched with respect to rain by about 0.3‰ , the extreme values being as low as 0.1‰ to 1.2‰ at the maximum in single events. Gat and Tzur (1967) applied the Craig-Gordon formula, Craig and Gordon (1965), to estimate the enrichment of the canopy reservoir in semi-arid conditions. They expected an overall enrichment in the throughfall to be about 2‰ , assuming that the next rainfall washes off the enriched residue from the canopy cover. In contrast to their simulation, all the rainfalls considered in this study are separated from the previous and the next storm by at least 10 hrs. Since the time for the canopy reservoir to dry out is about 5 h for Swedish conditions, Bringfelt and Hårsmar (1974), the possibility of extra enrichment from the previous rain's residue is ruled out in the present study at Uppsala. For the sake of illustration, a few

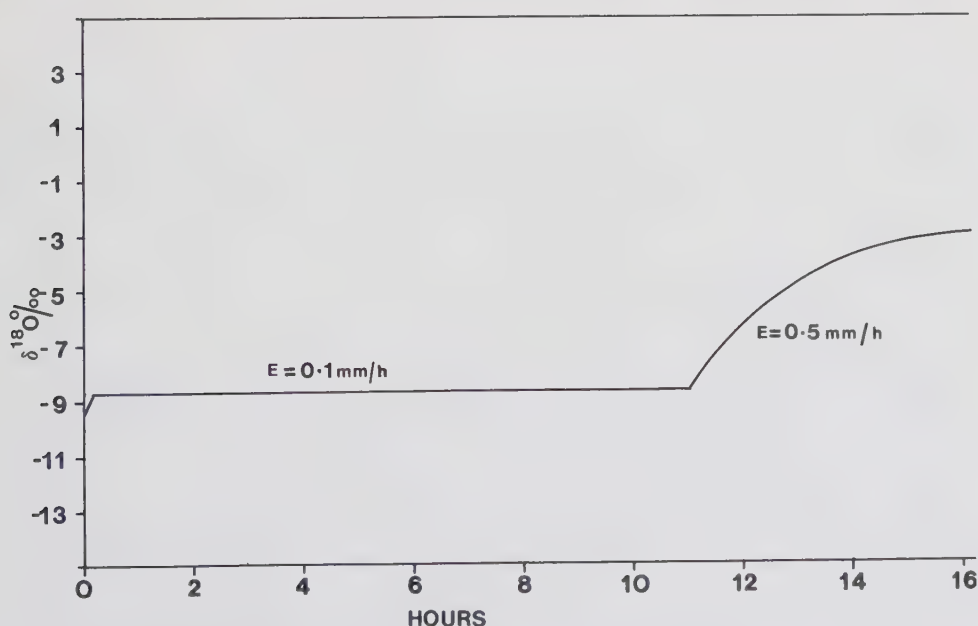


Fig.(7.5) Fractionation in the canopy water during and after a rain storm. Note the quick enrichment from -9.3 to -8.7‰ in the first hour during rain and the tremendous enrichment after the rain (curved part).

simulations on the fractionation of the canopy reservoir after the rainfall have been done.

After the cessation of rainfall, the evaporation is assumed to be 0.5 mm/h and the relative humidity about 80%. The curved part of Fig.(7.5) shows the enrichment of canopy reservoir after the storm. The evaporation continues until the reservoir is dried up. It is observed that the final δ value of the reservoir is tremendously high with regard to the initial δ value of rain. What fractionation of the reservoir is dripped as throughfall after the rain is not possible to determine from the available data from Uppsala. Hence it is difficult to estimate the overall enrichment in throughfall due to "washing off the residue" by the next storm.

On the other hand, the close agreement between calculated and observed δ values of the throughfall during the rain storm suggests that a major part of throughfall ($\approx 99\%$) is from canopy dripping during the event. If a substantial amount of throughfall is contributed by the canopy after the event, then the observed δ values of throughfall should be considerably higher than those observed experimentally.

7.5 Conclusions

From the above two studies it is apparent that the isotopic composition of throughfall differs from rainfall. This would certainly cause errors of estimation in studies involving water balance of a catchment by stable isotopes. It is clear that some storms may have variable isotopic distribution with time. Therefore it is imperative that, in future, studies should be made to measure even the differential isotopic nature of rain storms.

For studies on the separation of stream runoff using stable isotopes, it is important to modify the rain's isotopic composition in order to achieve higher accuracy. For an accurate prediction of throughfall's fractionation, the measurement of relative humidity during and after the rainfall is necessary. For better estimates of the canopy reservoir capacity, the free throughfall coefficient and the critical value of rain, it is essential to monitor throughfall and rainfall with a resolution of about 0.2 mm or less, rather than treating them on a cumulative basis. Such a method of sampling for single storm events can also give very accurate estimates of canopy evaporation during and after the storm.

8 ESTIMATION OF GROUNDWATER RECHARGE AND SOIL MOISTURE MOVEMENT BY ISOTOPIC TRACERS.

8.1 Introduction

Groundwater recharge estimation assumes a prime importance for water resource evaluations, urban water supply planning and agricultural practices etc. in regions where groundwater is a major source of available water. Recharge studies are of major interest for arids and semi-arids where water is a limiting factor for all developmental and sustained activities. The present threat of groundwater acidification in the European humid climates has further given an impetus to studies aimed at groundwater recharge evaluation.

Recharge can be estimated from long-term pumping tests, from fluctuations in groundwater level, from water balance computations and from soil moisture measurements etc. Recently isotopes (environmental and artificial) have been increasingly employed to determine groundwater recharge on local and regional scales.

The variations in the magnitude of groundwater recharge are enormous. In arids, it can be as low as 1 to 3 mm/year, Walton (1970), Allison et al. (1984), and in semi-arids it could vary from 30 to 100 mm/year while for glacial till in humid regions it can fluctuate from 90 to 670 mm/year, Walton (1970) and Eriksson (1980).

The hydraulically based methods involving monitoring of soil moisture transport below the active root zone are hampered by the complex relationship between hydraulic conductivity and hydraulic gradient in the unsaturated zone. The conventional methods also require a large volume of hydrological and meteorological data, i.e., precipitation, evapotranspiration, surface runoff and changes in moisture storage, etc. In the last decade, extensive mathematical theories have been developed by soil physicists to describe moisture movement under different sets of initial and boundary conditions. The basic principles of water infiltration in the unsaturated soil have been discussed in detail by Phillip (1969) in his state-of-the-art article. The theoretical treatments and numerical approaches employed by Freeze (1971), and Hornberger and Remson (1970) are noteworthy.

To avoid extensive computational time, semi-analytical solutions have been used for solving practical problems. In the numerical modelling of soil moisture movement, the unsaturated flow below the root zone is assumed to be governed mainly by gravity. The capillary gradients are considered to play a relatively minor role as the moisture content is thought to be equal to the soil field capacity or very near to it, with little variations. Generally a gravity wave is routed through the unsaturated zone and the time lag between the percolation at the root zone and the eventual recharge is computed. Storm and Refsgaard (1980) used a finite difference method for this purpose. Analytical solutions can be sought from the kinematic wave theory using the modifications suggested by Colbeck (1974, 1975, 1978) for meltwater percolating through a snowpack and was applied to hillslopes by Beven (1981, 1982a, b).

Predictions of the actual processes in the field require a proper knowledge of the hydraulic characteristics of the soil including the functional relationships between hydraulic conductivity and matric suction with respect to moisture content of the soils. The spatial and temporal variations of the above further complicate the picture. With the advent of neutron moisture meters and gamma transmission gauges, the problem of monitoring soil moisture content in situ has been practically solved but for the surface layers, where neutron gauges are not very accurate. A combined use of nuclear gauges (neutron or gamma transmission sondes) and the conventional hydraulic methods has become a standard technique to monitor soil moisture movement, specially in dry land farming for the estimation of irrigation losses below the root zone, Arora et al. (1977).

In the last two decades, tracer methods have been employed to study soil moisture movement and groundwater recharge. Tracer technique has the advantage that old soil water can be differentiated from the relatively fresh percolating water and even the particle velocity of water can be determined. This field of research has become so vast that it requires a separate discussion and the next section is devoted to it.

8.2 Radiotracers in estimations of groundwater recharge-a brief review

Zimmermann et al. (1966) developed a direct method for estimating the rate of soil moisture movement and vertical groundwater recharge by using radioactive tracers such as tritiated water. The principle of the tracer method is that soil moisture

is tagged or labelled artificially with an isotopic tracer in a horizontal plane below the root zone. During the course of infiltration, the tracer is carried along with the moving soil moisture. Field studies by Zimmermann et al. (1967a, b) and Blume et al. (1967) have shown, in homogeneous soils, that

- a) soil moisture cannot bypass the tagged layer in either direction in the vertical.
- b) the downward displacement of the tagged layer is like a moving piston.

The rate of soil moisture movement is determined from the temporal displacements of the tagged layer. The above method has been applied in various field conditions, e.g. in the alluvial formations in India, Datta and Goyal (1977), Bahadur et al. (1977b) and Athawale et al. (1980). In the above-mentioned experiments, the broadening of the peak of the introduced tracer was of the same magnitude as expected by molecular diffusion only. Experiments conducted in the alluvial tracts of north India by Bahadur et al. (1977b) also showed that the broadening of the tracer peak was comparable to the spread by molecular diffusion. When the flow is slow, the lateral mixing, mostly from molecular diffusion, in rather homogeneous soils between moisture packets having different flow velocities is quite effective, thus indirectly counteracting vertical dispersion.

The major advantage of tritium tagging is that it gives direct measurements of recharge and can be applied in remote areas for which meteorological or hydrological data are not available nor monitored. Other soil parameters, e.g. hydraulic conductivity and matric suction and other meteorological parameters, are not needed either. Also in a broader sense, since tritiated water has the same chemical properties as ordinary water, it is supposed to move freely with soil moisture.

Groundwater recharge has also been estimated using environmental tritium. In the atmosphere, tritium is produced by the interaction of cosmic ray neutrons with ^{14}N in the following manner



The production rate of environmental ^3H from cosmic rays (before the beginning of thermonuclear explosions) seems to have

followed a steady pattern and is about 0.25 tritium atom/sec/cm² of the earth's surface. The cosmogenically produced tritium is found entirely in atmospheric vapour and is brought down to earth's surface by precipitation at a constant rate. However, since 1952 with the dawn of the thermonuclear tests in the atmosphere, tritium concentrations in precipitation suddenly increased and reached a record-high concentration in 1963-64 in the northern hemisphere. In Sweden the peak concentration of bomb tritium in 1963 was about 2100 Tu. 1 Tu is equal to 1 atom of ³H in 10¹⁸ H atoms, or 0.12 Bq/litre water.

The use of environmental tritium is based on the fact that the fate of ³H in precipitation is the same as that of precipitated water. In case of homogeneous aquifers where it can be assumed *a priori* that the younger infiltrating water pushes down the older water in a piston-flow pattern, the concentrations of bomb tritium in soil moisture will reflect its concentrations in precipitation. In reality, the ³H concentrations in the soil profile will be to some extent moderated due to dispersion and molecular diffusion. However, the 1963-64 peak concentrations of bomb ³H could be identified in the unsaturated zone, where the groundwater was deep enough, as late as 1970. Münnich et al. (1967) and Sukhija (1972, 1976) have used bomb-released tritium for the evaluation of groundwater recharge in Europe and India respectively. One of the approaches is, that the amount of water from soil surface to the soil depth, where the 1963-64 tritium peak is located, is the measure of recharge until the time of investigation.

In other words, if Θ is the average volume moisture content of the soil from the surface down to the depth z where the 1963-64 peak ³H concentration is found, then the recharge R till the time of investigation is

$$R = \int_{\text{surface}}^{z\text{-peak}} \Theta \cdot dz \quad (8.1)$$

The other method is based on the ³H balance between ³H in fall-out (i.e. ³H in precipitation) and accumulated ³H in the unsaturated zone. The ratio of ³H in the soil to total ³H input from precipitation is the recharge as a fraction of precipitation. In its simplified form, the method works in the following manner. The total ³H input since 1952 in precipitation can be written as

$$T_p = \sum_{1952}^i T_i P_i \quad (8.2)$$

where T_i is the tritium concentration in precipitation in month i corrected for radioactive decay to the time of observation and P_i is the corresponding amount of precipitation.

Similarly the total amount of tritium in the soil up to a depth z where tritium concentration approaches pre-1952 ^3H concentrations is thus

$$T_s = \sum_{j=1}^z T_j \Theta_j \quad (8.3)$$

where T_j is the amount of ^3H in the soil section, j , and Θ_j is the volume moisture content of that soil section. T_s in fact represents the total percolation in the soil after evapotranspiration and surface runoff. Then

$$T_s/T_p = R \quad (8.4)$$

is the recharge as a fraction of precipitation.

It is assumed that the tritium concentration of water lost as evapotranspiration and surface runoff is equal to the mean concentration of tritium in precipitation for the observed period.

The environmental ^3H method was relatively more useful only until the mid-1970s. Most of the thermonuclear tests after the 1960s were confined to underground sites and the concentration of ^3H since then has dropped off sharply. On the other hand, most of the bomb ^3H has by now mixed with the groundwaters and the soil profiles have more or less a constant concentration of ^3H . Hence, for the present time, the utility of bomb ^3H for the direct estimation of groundwater recharge is very limited.

Apart from the use of ^3H both as an artificial and environmental tracer for groundwater recharge studies, other radiotracers like ^{60}Co in a complex form have been used in a pilot study, Nair et al. (1980). They have tried ^{60}Co as $\text{K}_3^{60}\text{Co}(\text{CN})_6$ in laboratory as well as in field experiments and compared the results with tritiated water and found a good agreement. Their method is that they injected $\text{K}_3^{60}\text{Co}(\text{CN})_6$ around an access tube at several points in a circle at a suitable depth. The tracer forms a ring-like layer around the access pipe and its peak

concentration is determined at regular intervals by lowering a gamma-scintillation detector at various depths. They found no significant differences in the behaviour of the ^{60}Co complex and tritiated water, in terms of retardation in the soil profile. However, the ^{60}Co -EDTA (Ethylene Diamine Tetra Acetic Acid) complex was strongly retarded in comparison to the cyanide complex. On the other hand, Knutsson and Forsberg (1967) reported ^{51}Cr -EDTA to behave as an ideal tracer even at low concentrations. Still, the method of gamma-emitting tracers has to show its versatility in different geological settings. On the other hand, the use of stable isotopes of water (i.e. ^{18}O and D) for a direct estimation of groundwater recharge has not been seriously attempted so far.

8.3 Use of stable isotopes for estimation of groundwater recharge and rates of soil moisture movement.

Stable environmental isotopes (^{18}O and D) separately and in conjunction with environmental ^3H have been used in groundwater recharge studies in a limited sense. Often such studies were aimed at the identification of regional recharge-discharge zones, Gonfiantini et al. (1976). ^{18}O and D have also been used as indicators of recharging events, i.e., recharge by direct infiltration of rains and from floods or through the intermediary of stagnant water pools, Levin et al. (1980). Very few studies have been reported where direct estimations of groundwater recharge were obtained by stable isotopes. Eriksson (1976) made an interesting use of chloride in Delhi groundwater to estimate annual recharge. Assuming that chloride in groundwater is mainly air-borne and percolates through the soil matrix along with precipitation, he estimated the recharge to be about 33 mm/year.

In a pilot study in the Pilat sand dunes, Thoma et al. (1979) reported the use of deuterium as a tracer for groundwater recharge estimations. They found oscillations in the D-content of the soil profile which were thought to reflect the seasonal variations of D in precipitation. But the authors refrained from giving any values for groundwater recharge.

In the arid and semi-arid regions of Australia, Allison et al. (1984) found an empirical indication that the isotopic deviation of groundwater relative to the meteoric line (on the δD - $\delta^{18}\text{O}$ space) was inversely proportional to the square root of groundwater recharge. However, the field data were not enough to confirm this view.

8.4 Moisture movement and recharge estimates - some theoretical considerations

In the course of water infiltration, an artificial or environmental tracer is carried along with the soil water. The position of the peak tracer concentration can be monitored in the soil profile. From the temporal displacement of the tracer, a percolation rate or a moisture flux, and for certain conditions the ground-water recharge, can be estimated provided the measurements are taken below the root zone and all water movements are directed downwards. The principle of how percolation rates are determined from tracer monitoring is illustrated in Fig. (8.1). After the tracer injection (say tritium), the peak concentration is at depth z_1 and after a time Δt it is found at depth z_2 . Provided that the downward movement can be considered as piston flow so that no vertical mixing, except for molecular diffusion takes place during the downward movement, the particle velocity or displacement is

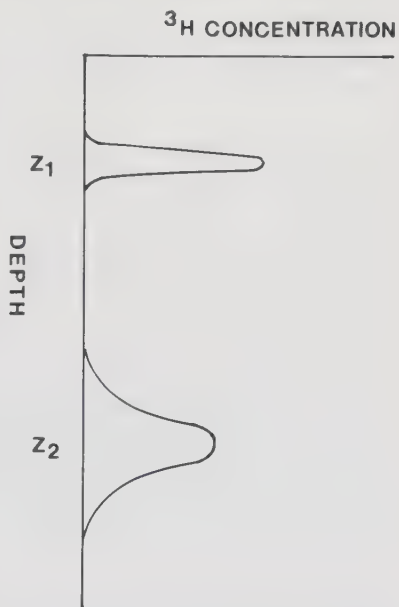


Fig.(8.1) Schematic diagram of tracer concentration at depth z_1 and after time Δt at depth z_2 .

$$v = \frac{z_2 - z_1}{\Delta t} \quad (8.5)$$

The soil water, m , that passes the lower depth z_2 during the period Δt between the two observations is

$$m = \int_{z_1}^{z_2} \Theta(z, 0) dz \quad (8.6a)$$

where Θ is average soil moisture at time zero (at the first observation) after reduction of the interstitial moisture, which is attached irreducibly to the very fine soil particles. This residual moisture content is generally believed to be negligible, except maybe for very fine soils.

The average moisture flux, q , through the lower depth z_2 over the period Δt is

$$q = \frac{m}{\Delta t} = \frac{1}{\Delta t} \int_{z_1}^{z_2} \Theta(z, 0) dz \quad (8.6b)$$

The moisture flux that passes below the root zone will eventually contribute to groundwater recharge, but the exact time when the groundwater is recharged cannot be found by this method.

The above is true when the peak positions at z_1 and z_2 are such that they have already passed the root zone and the moisture between z_1 and z_2 cannot be lost by evapotranspiration. The tritium peaks broaden out with time due to dispersion and molecular diffusion but the use of centre of gravity to determine the peak position reduces the experimental error considerably.

However, in the case of ^{18}O profiles the situation is not so well defined as in the tritium peaks. One has to identify the positions of ^{18}O -depleted or enriched soil moisture. A simplified graphic representation is given in Fig.(8.2), where z_A is the average depth of the ^{18}O -depleted layer which is displaced to depth z_B after a time Δt .

If the time period, Δt , between the two observations is a full year, the moisture flux corresponds to the yearly recharge. However, for calculating annual recharge, sometimes one single observation can be used. The soil moisture is measured between two levels, say z_1 and z_3 , at which the soil water can be identified to originate from two events, preferably snowmelt, one year apart in time. Since the environmental ^{18}O concentration is depleted in meltwater in comparison to summer and autumn rains, Fig.(8.3), measurement of ^{18}O in a soil profile at one single occasion can be sufficient for estimating the percolation or the groundwater recharge. Mathematically, the annual percolation, R , is given by

$$R = \int_{z_1}^{z_3} \Theta(z) dz \quad (8.7)$$

where Θ is the average soil moisture at the specific time when the contribution from the first and second year is found at the depths z_1 and z_3 , respectively.

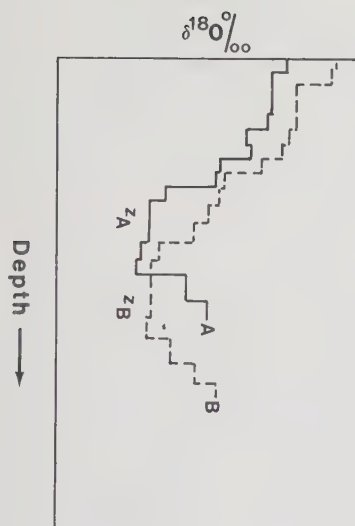


Fig.(8.2) Schematic diagram of ^{18}O of soil moisture, showing snowmelt (i.e. ^{18}O -depleted) moisture at depth z_A which moves to depth z_B after time Δt .

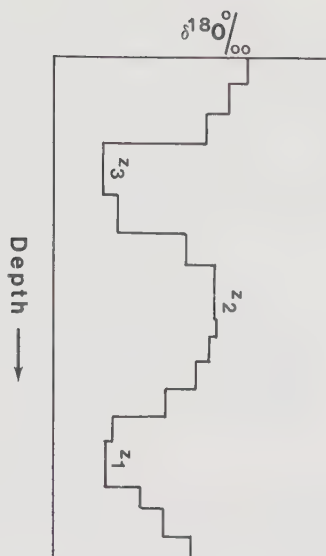


Fig.(8.3) An illustration of seasonal fluctuations of ^{18}O in precipitation preserved in the soil moisture. Depleted moisture derived from two consecutive years' snowmelt found at depths z_1 and z_3 while moisture from summer rains is found at depth z_2 .

8.5 Oxygen-18 as a tracer for recharge estimations: field studies

The seasonal variations of ^{18}O in precipitation have been traced in the soil moisture with the aim to estimate vertical ground-water recharge and moisture movement in Swedish glacio-fluvial deposits and glacial tills.

It has been observed that winter and summer precipitation in Uppsala differ in their ^{18}O content by about 6-8‰, Fig.(8.4). During snowmelt, the meltwater which is of relatively light isotopic composition acts as a source of ^{18}O depleted water and during infiltration in the soil, labels or tags the soil moisture with low ^{18}O content. After the melt period, early summer rains having relatively high ^{18}O content push down the ^{18}O depleted meltwater, which in turn further pushes down the older moisture (having high ^{18}O content) contributed by the previous years' summer rains. Thus the meltwater forms an ^{18}O -depleted tagged layer which is sandwiched between the older and the

younger waters both having relatively high ^{18}O . The rate of the downward displacement of the tagged layer gives direct information about the rate of soil moisture movement. Under some field conditions in Uppsala where the water table was deeper than 3 m, infiltrated meltwater from two consecutive melt periods has been traced in the unsaturated zone providing estimates of annual recharge.

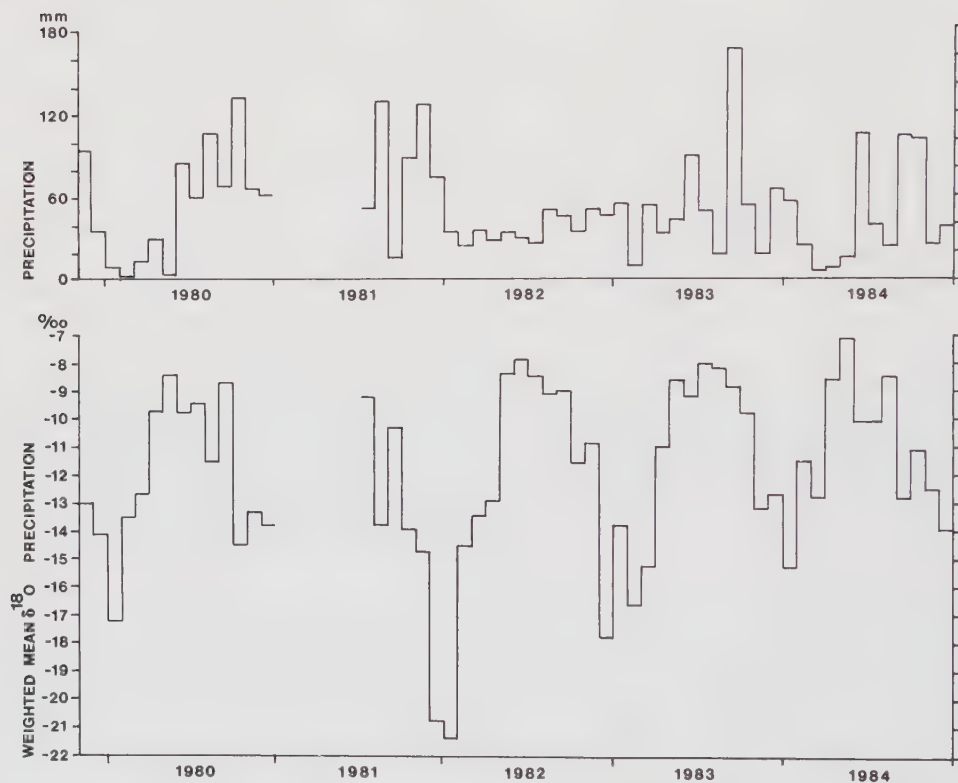


Fig.(8.4) Weighted monthly mean $\delta^{18}\text{O}$ and amount of precipitation at Uppsala, from 1980 to 1984.

Initially, ^{18}O profiles of soil moisture were obtained from the sands in Uppsala, but later on, as the technique proved to be successful, moraine formations in Kloten and Örbyhus were also included in the studies. The field site at Uppsala was also injected with HTO below the root zone in small plots and the temporal displacements of the ^3H -tagged layers were compared with that of ^{18}O -depleted layers to check the accuracy of the ^{18}O method.

8.6 Description of sites

Uppsala

This site is situated on the western flank of the Uppsala esker. The area is covered by a shallow deposit of post-glacial sand and fine sand. Underlying the post-glacial deposit is an old Archaean formation of granite. Occasional outcrops of the bedrock occur in the area. The homogeneity of the soil profile in the vertical is disturbed by the occurrence of thin clay lenses at certain depths. The water table at the site is below 3.5 m depth. The occurrence of clay lenses was seen at 120 to 230 cm depth. Yet another soil profile at the same site was rather free from clay.

Kloten

Kloten is situated about 140 km west of Uppsala. The Kloten moraine consists of unsorted material varying in grain size from big boulders to material crushed down to the size of clay. The soil material is coarser near the surface than farther down, Lundin (1982). The water table varied from 0.6 m to 2 m at the sampling site.

Örbyhus

The site is located 42 km north of Uppsala. The main physiographic criteria are similar to those at the Kloten site, i.e. topographically one could expect a deep water table and little or no lateral flow in the unsaturated zone. The sampling was carried out on the top of a small moraine ridge. The top soil is sandy-gravelly till, which is wave-washed in top layers, whereas the deep soil contains sand and silt.

8.7 Experimental methodology

Tritium injections

Tritium was injected as HTO in 2 x 2 m plots in Uppsala at 30 cm below the soil surface under the snow cover just before the melt period began. For a uniform labelling of soil moisture, HTO injections were made in a square grid, the injection points being at 10 cm interval. A stainless steel tube (diam. 10 mm) was hammered to 30 cm below the soil surface and then a brass

tube (diam. 6 mm) was lowered into the hole and 10 ml HTO (18.6×10^3 Bq/ml) was injected by a constant volume pipetting device attached to the brass tube.

8.7.1 Field sampling of soil moisture

Soil coring

In the sandy formations at Uppsala, soil coring by a Veihmeyer tube was very successful even to a depth of 3.5 m. 10 cm long soil cores were taken at Uppsala. For ^{18}O analysis, cores were taken about 5 m away from the edges of the tritium-tagged plot. Soil cores were immediately stored in stainless steel cans fitted with airtight caps. These samples were later stored in the laboratory, frozen to -30°C before moisture extraction. To test that the storage of soil samples in steel cans does not introduce any fractionation in ^{18}O , oven-dry soil was mixed with a known amount of water of known ^{18}O content and kept for two weeks at room temperature. Some of the cans were stored in a freezer at -30°C . The analysis after two weeks showed that no fractionation occurred in frozen cans, while some of the cans kept at room temperature showed fractionation in ^{18}O by about 0.4‰.

Soil sampling from pits

The glacial tills cannot be sampled by the coring method because of a large assortment of pebbles and small boulders. Thus for the morainic material at Kloten and Örbyhus pits were dug and the soil samples were obtained at 10 cm intervals, by scraping the walls of the pit and pressing the cans against the pit-walls. At Kloten the pit size was 190 x 80 cm and sampling was done to a depth of 200 cm. At Örbyhus a digging machine was employed and a huge pit (6 x 6 m) was dug down to 4.75 m.

Soil-air suction

Thoma et al.(1979) have described a method for suction of soil moisture from desert sands. Their method has been used here with some modifications. The only disadvantage is that soil moisture content cannot be obtained directly, and one has to resort to gravimetric or neutron scattering methods.

A probe, Fig.(8.5), consisting of an inner tube with a perforated lower section terminating in a pointed end and an outer

tube with a mechanism for covering and uncovering the perforated section, is driven into the tritium-free and the tritium-tagged plots. The inner and outer tubes are isolated from each other by a rubber O-ring. Once the probe is driven into the soil down to the desired depth, the outer tube is lifted by rotating the handle to open the inner perforations.

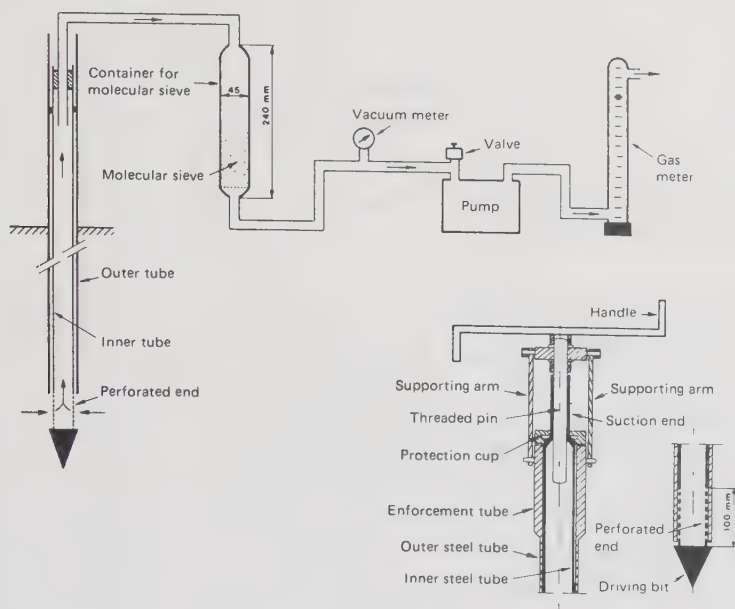


Fig.(8.5) Schematic diagram of field soil-air suction apparatus. (From Saxena & Dressie, 1984.)

The inner tube is then connected to a Pyrex glass cylinder containing 150 g 4 Å molecular sieve and soil air is sucked through the sieve by pumping for about 10 minutes. The vacuum meter is used to check for leakage in the system, and the flow can be regulated by a valve and a flow meter. The moisture-laden molecular sieve bed is transferred to bottles for later moisture extraction in the laboratory. Before proceeding to the next level, the outer tube is lowered to cover the perforations and the whole tube is again hammered down.

To ensure that enough moisture has been absorbed in the molecular sieves, the sieve cylinder in the dry state is weighed by a feather balance in the field and is weighed again after moisture absorption. If the difference in weight is more than 5 g, the next step is executed, if not, suction is continued for some

time more. In the relatively moist conditions in Uppsala, 10 minutes were enough to obtain ≥ 7 g of absorbed moisture. The same sieves can be reused after they have gone through the desorption process. For a quick sampling, pre-weighed dry sieves are kept in airtight bottles and the cylinders are filled with sieves in the field. The above method is well suited for relatively dry and friable soil conditions where soil coring could be a problem as soil can easily slip through the coring tube. On the other hand, at depths where soil moisture is $\geq 15\%$ (vol.), it has been observed that water in liquid form is sucked up in the sieves which disturbs the soil moisture regime.

8.7.2 Laboratory extraction of moisture from soil cores or samples

In the present study, moisture extraction from soil cores is done by vacuum distillation at $50\text{--}60^\circ\text{C}$, Fig.(8.6). Cans containing the soil cores are weighed and placed in desiccation chambers fitted with 55 W disc-shaped heating elements, which are temperature-regulated by a relay. Each desiccation chamber is connected to two glass vapour traps put in series to ensure complete moisture recovery. The glass traps are evacuated before their placement in a cooling chamber containing alcohol kept at -60°C by a compressor. During evacuation of the traps, the desiccation chambers are kept closed by a valve. About 20 minutes are needed to cool down the traps, and at this stage the chambers are slowly opened and heating is started. About 5 hours are required to remove all moisture from the soil cores.

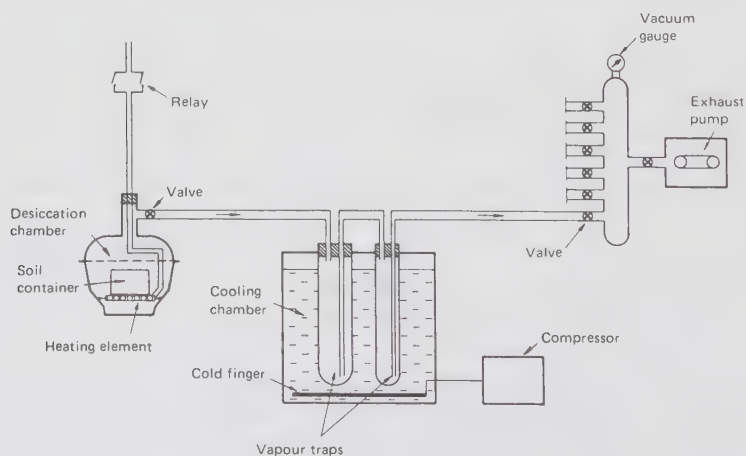


Fig.(8.6) Schematic diagram of laboratory extraction of moisture from soil cores. (From Saxena & Dressie, 1984.)

In this set-up, six soil cores can be distilled simultaneously. The weight loss of the cans is checked against the weight gain of the traps. During standardization of the technique, oven-dried soil was mixed with a certain amount of water of known ^{18}O content. It was observed that the recovery of moisture is almost 100% and practically no fractionation of ^{18}O occurs during storage and extraction. The same procedure was repeated with oven-dried soil mixed with a certain amount of tritium. No loss of tritium during extraction was observed. It may be mentioned that tritium does not suffer from fractionation effects at the activity level used in the injections. This technique can also be used for extraction of natural tritium from soil cores. The error in ^{18}O measurements is $\pm 0.1\%$ and the results are expressed as $\delta^{18}\text{O}(\text{SMOW})$, whereas tritium activity is given in counts/min. per ml.

Various methods are in use for moisture extraction from soil cores or soil samples. Allison et al. (1983) have used azeotropic distillation with toluene. The soil sample is put in a flask containing toluene and is heated to about 98°C . Water vapours are lead through a tube fitted at the top and are collected as liquid water at the other end. To remove traces of toluene from water, a lump of paraffin wax is added to the water-toluene mixture and warmed to about 50°C . In their set-up, the process takes about 30 minutes for sandy samples and about 2 hours for clay material. Darling et al. (1982) have reported the use of centrifugation, i.e. the displacement of pore fluid by an immiscible liquid. They have used Arclone, a cheap fluoro-carbon liquid and found it to be specially suitable for silt and clay grade material. However, this method is not applicable when the soil moisture is lower than 10% by weight. In the present experiment vacuum distillation has been preferred to the other available methods. The soil samples are heated at relatively lower temperature than those used by other workers, e.g. Darling et al. (1982). In the limit of high temperatures, say 200 to 300°C , and at very low pressures there is a chance that the water of crystallisation of the soil particles might be released which may change the real isotopic content of the soil moisture. Such a change has not been observed by Darling et al. (1982) who used high temperatures (300°C) for samples of chalk. However, the effect of high temperatures on sandy and moraine samples has not been checked so far.

Soil moisture determination

The above method of moisture extraction also yields direct measurements of the moisture content (by weight) of the soil samples. The steel cans containing moist soil samples are weighed before and after extraction of moisture. The difference in weight is the moisture present. Since the weight of empty cans is known, the weight of dry soil is also determined. From the bulk density of each 10 cm soil section, the volumetric moisture content is calculated. For bulk density measurements, a pit was dug to 150 cm depth in steps of 10 cm. Soil samples of constant volume and geometry were obtained by pressing the cans in the soil at 10 cm intervals. The standard method of oven drying for 24 hours at 105°C was used for drying the soil samples.

Moisture extraction from molecular sieves

The moisture-laden molecular sieve-bed is transferred again to Pyrex glass cylinders, five of which can be placed in a specially designed oven maintained at 450°C. The released vapours are collected in traps cooled to -60°C in the same way as for vacuum distillation of soil cores. In this case, the oven replaces the desiccation chambers. It takes about 3 hours to extract all moisture. The last remnants of moisture from the system are driven out by flushing dry nitrogen for about 15 minutes. The theory of molecular sieves and related information has been reported in detail by Thoma et al. (1979). The present system is an improved version, as it allows extraction from five samples simultaneously and does away with metal cylinders (as sieve containers) which had a cumbersome system of heating and cooling.

8.8 Results and discussions

8.8.1 Comparison of ^{18}O and ^3H methods

The rates of soil moisture movement during different periods of 1982 have been obtained from the temporal displacements of the tritium tagged and ^{18}O depleted moisture. The average peak positions, their displacement with respect to time, rate of moisture movement and moisture fluxes are shown in Table (8.1).

Table (8.1) Rates of soil moisture movement (i.e. the water particle velocity) and moisture fluxes, estimated by oxygen-18 and tritium tracer methods, in plot U₁ Uppsala.

Period	Average peak positions (cm)		Displacement (cm)		Average soil moisture (vol %)		Rate of moisture movement (mm/d)		Moisture flux (mm/d)	
	¹⁸ O	³ H	¹⁸ O	³ H	¹⁸ O	³ H	¹⁸ O	³ H	¹⁸ O	³ H
12 March to 4 May 1982	40-70	35-65	30	30	16.8	17.4	5.7	5.7	0.96	0.99
4 May to 22 July 1982	70-100	65-95	30	30	17.3	17.3	3.8	3.8	0.66	0.66
22 July to 24 Sept 1982	100-130	95-115	30	20	10.8	11.5	4.7	3.1	0.51	0.36
4 May to 24 Sept 1982	70-130	65-115	60	50	14.1	15.9	4.2	3.5	0.59	0.56

The temporal displacements of the ³H peaks and the ¹⁸O-depleted layers agree fairly well. The water particle velocity is comparatively higher just after snowmelt, i.e. ≈ 5.7 mm/d, Table (8.1), but later decreases a little, being ≈ 3 to 4 mm/d.

The rates of moisture movement obtained by the two methods are exactly the same during March to May and from May to July 1982. The particle velocities and fluxes are relatively different in both methods during July to September, because of the field variability and relatively large broadening of the ¹⁸O-depleted layer, which makes it difficult to judge its true average position. The moisture fluxes through different levels are also very similar, being almost 1 mm/d after snowmelt and ≈ 0.5 mm/d later on.

The tritium profiles, see Fig.(8.7a to 8.7e), relative to the ¹⁸O profiles are sharp in the beginning, but broaden with the passage of time, as was also the case with ¹⁸O-depleted moisture layers. Curve c in Fig.(8.7) shows a comparison between soil coring and soil-air suction methods, used for the tritium sampling. The centre of gravity of the tritium distributions is almost the same in both cases, though the tritium peak shape from the suction method is comparatively broader. From this field experience of soil air suction it is inferred that the method can be useful for dry soil conditions where soil coring becomes difficult due to collapsing of the dry cores. For

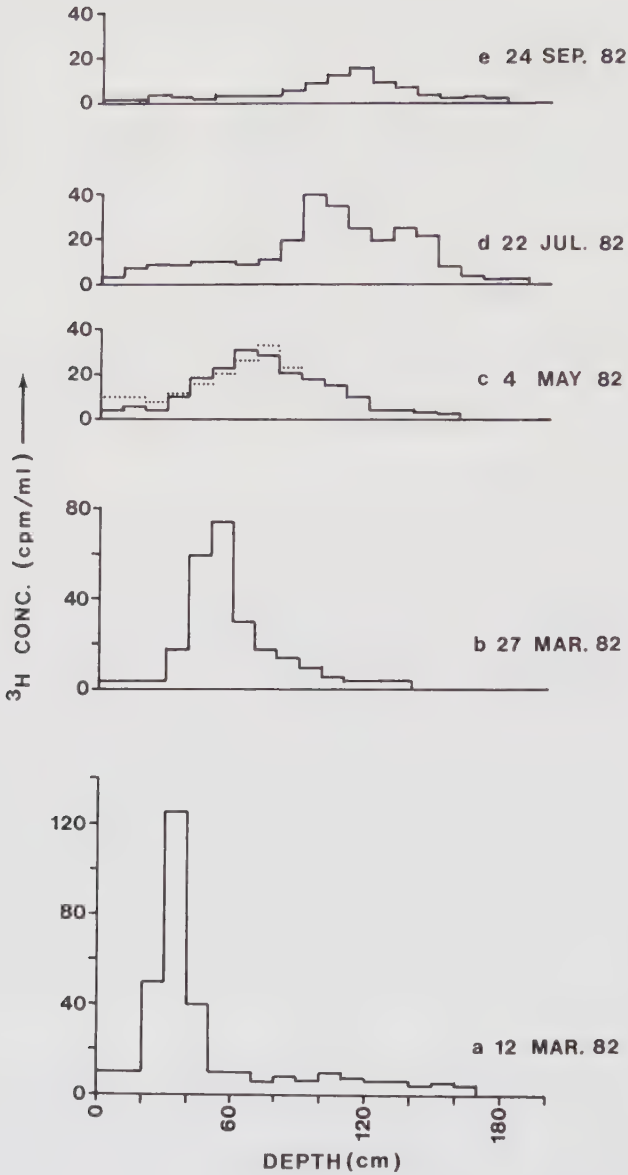


Fig.(8.7) ^3H concentration of soil moisture at Uppsala, plot U_1 . Injection depth of HTO was 40 cm below soil surface on 12 Feb. 1982. Dotted profile observed in May is from soil-air suction method. Full lines denote profiles obtained by coring method.

Swedish conditions, where soils are moist enough, the coring method is more convenient and efficient. The main disadvantage of the suction method is that it does not give information on the soil moisture content and is more time consuming.

8.8.2 Moisture movement and estimation of seasonal recharge by ^{18}O

Uppsala

Before the beginning of snowmelt in February 1982, the depth of the snow pack was 55 cm, the water equivalent was 137 mm and the average $\delta^{18}\text{O}$ of the snowpack was -16.6‰ . The first soil sampling was done on 13 February 1982. Fig.(8.8) shows the ^{18}O profile of soil moisture at Uppsala in February 1982.

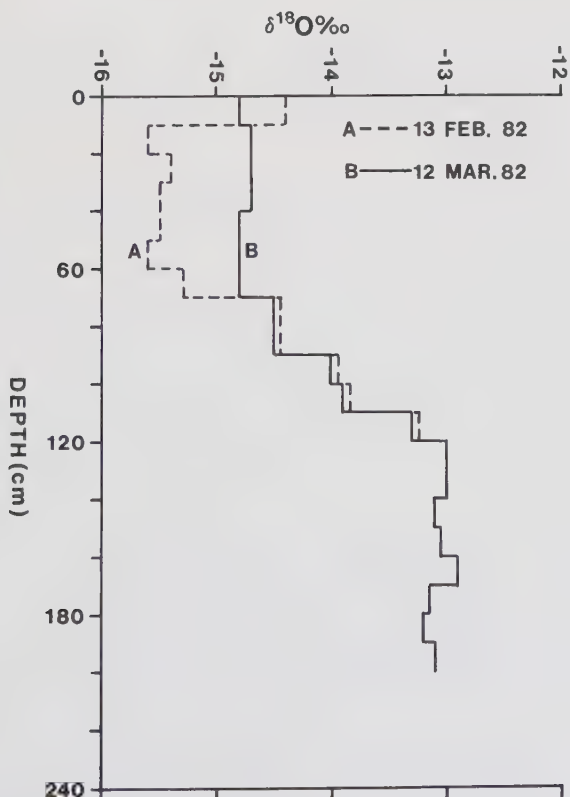


Fig.(8.8) ^{18}O profiles of soil moisture in plot U_1 , Uppsala, February and March 1982.

The soil moisture ($\delta^{18}\text{O} = -15.4\text{‰}$) extending down to 70 cm depth, profile (A), was due to melting of early snow (October-December 1981), the weighted δ value being -15.6‰ . The ^{18}O profile (B), observed in March 1982 when melting had just begun, showed that the depleted moisture front had advanced to 90 cm, but at greater depths the moisture content as well as the $\delta^{18}\text{O}$ distributions remained unchanged. On making a water balance from 0-100 cm depth (as the moisture and ^{18}O contents remain unchanged below 100 cm), it was found that the moisture content had increased by 8.9 mm in March 1982. The isotope and water balances show that the weighted $\delta^{18}\text{O}$ of soil moisture in March 1982 between 0-100 cm should be -14.6‰ which agrees fairly well with the observed (weighted) $\delta^{18}\text{O}$ of soil moisture which was -14.7‰ . The above is an illustration of $\delta^{18}\text{O}$ profiles of the soil moisture just before and after the onset of snowmelt and some conclusions that can be drawn therefrom.

In these calculations it has been assumed that a loss of 7.5 mm from the soil from February to March is by transpiration only, as this process does not cause any fractionation in ^{18}O , Zimmermann et al. (1967a).

From the ^{18}O profile from a single soil sampling during 1982 and 1983, annual percolation or the "eventual recharge" has been estimated. The soil moisture was identified to originate from the melt periods of 1981 and 1982 spring and can be clearly identified in the ^{18}O profiles observed in May 1982, Fig.(8.9). The first ^{18}O -depleted moisture layer (average depth 70 cm, profile C) represents snowmelt 1982, and the second layer with relatively higher ^{18}O content is derived from summer rains 1981. The third moisture layer which is also depleted in ^{18}O (average depth 235 cm) is due to the contribution from 1981 melt period. The total soil moisture (280 mm using Eq.8.7) present between these two ^{18}O -depleted layers is that water which entered the soil since the 1981 snowmelt and is the percolation between the melt periods of 1981 and 1982, Table (8.2). This percolated moisture will eventually reach the groundwater at some later date and can be termed as recharge between snowmelt 1981 and 1982.

The ^{18}O profile of soil moisture observed in July 1982 is shown in Fig.(8.9), profile D. The first ^{18}O -depleted moisture layer is found at average depth 100 cm, being displaced by 30 cm since May 1982. The second ^{18}O -depleted layer, average depth 270 cm, had been displaced by 35 cm. The amount of moisture entering the soil between snowmelt 1981 and 1982 is 272 mm, Table (8.2).

This is in close agreement with the estimate of recharge from profile C, taken in May 1982. Soil moisture sampling in September 1982, Fig.(8.10), did not yield a well defined ^{18}O profile, but the trend showed that the moisture continued to move downward. The poor resolution in the ^{18}O distribution is due to field variability and will be discussed in the later sections.

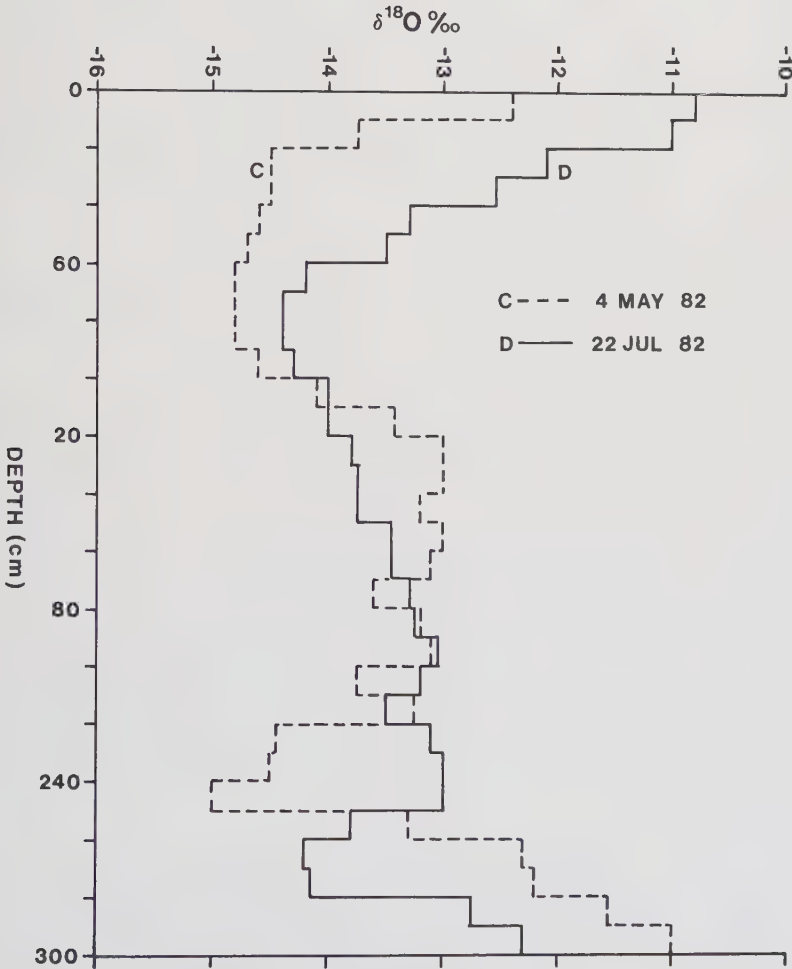


Fig.(8.9) ^{18}O profiles of soil moisture in plot U_1 , Uppsala, May and July 1982.

Table (8.2) The annual percolation or recharge and average rate of soil moisture movement (i.e. the water particle velocity). Profiles C to K are from Uppsala, while profiles P and R represent Kloten and Örbýhus, respectively.

Period	Name of profiles	Average position of ^{18}O -depleted or enriched moisture layers (cm)	Average soil moisture (vol %)	Distance between depleted or enriched moisture layers (cm)	Rate of moisture movement (mm/d)	Percolation/Recharge (mm)	% of pre-cipitation
Spring 1981 to 1982	C	70 - 235	17.0	165	4.5	280	41.0
Spring 1981 to 1982	D	100 - 270	16.0	170	4.6	272	40.0
Summer 1981 to 1982	G	70 - 240	19.2	170	4.6	326	49.0
Spring 1982 to 1983	J	85 - 190	18.0	105	2.9	189	42.0
Spring 1982 to 1983	K	140 - 240	19.0	100	2.7	190	42.0
May 1982 to June 1983	C - J	70 - 190	18.1	120	3.0	217	47.0
July 1982 to Aug 1983	E - K	115 - 240	20.0	125	3.2	250	48.0
Spring to Autumn 1983	P	40 - 150	17.8	110	5.8	196	-
Summer 1982 to 1983	P	60 - 220	16.6	160	4.4	266	38.0
Spring 1983 to 1984	R	140 - 400	10.0	260	7.1	260	-

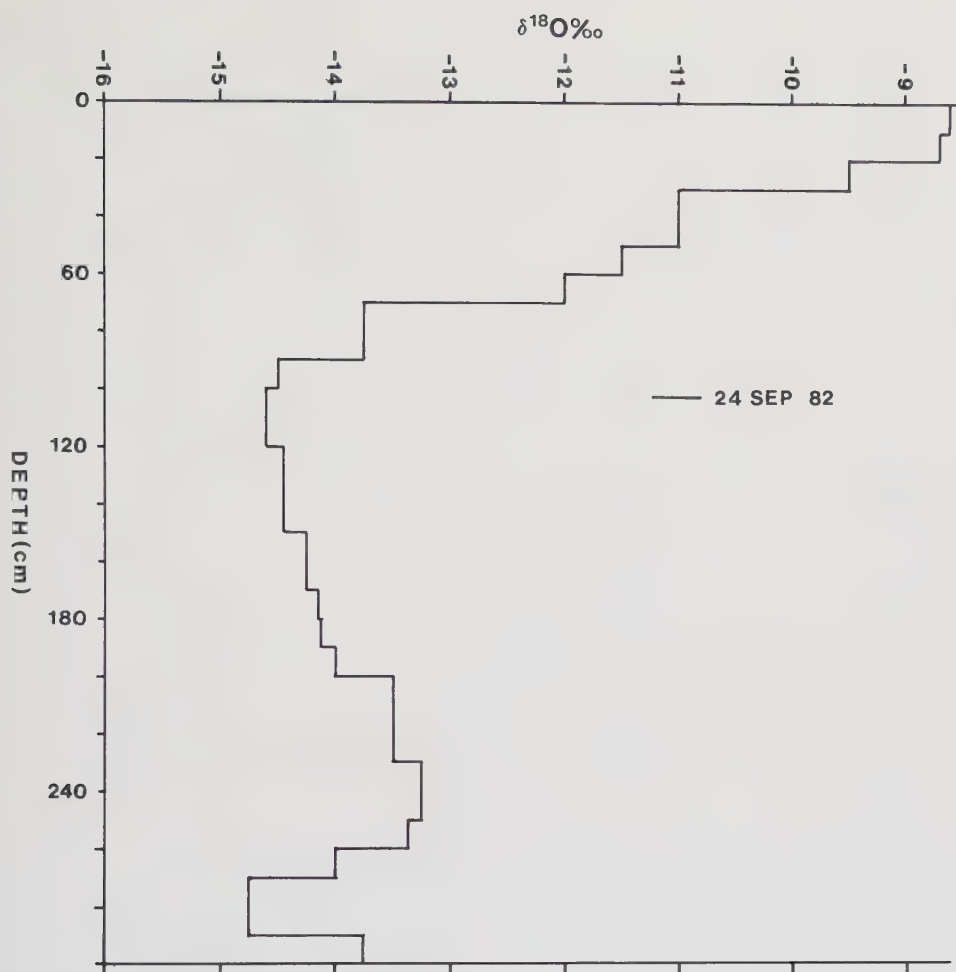


Fig.(8.10) ^{18}O profiles of soil moisture in plot U_1 , Uppsala, September 1982.

In July 1982, sampling was extended to yet another plot, U_2 , 10 m away from plot U_1 . The ^{18}O profiles in plot U_2 , Fig.(8.11), are well defined. Thus the temporal displacements of the ^{18}O -depleted layers could be determined more accurately as compared to plot U_1 . After September 1982, plot U_1 was abandoned on account of its extreme exploitation by corings and soil moisture suction.

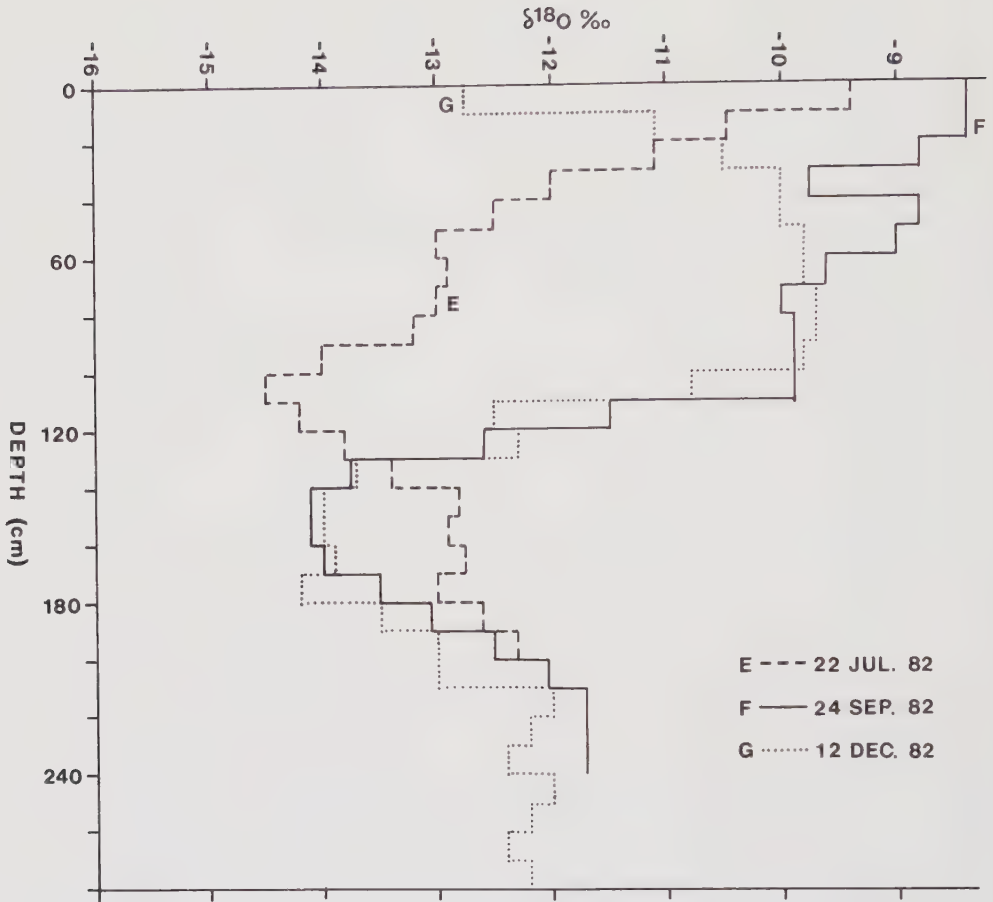


Fig.(8.11) ^{18}O profiles of soil moisture in plot U_2 , Uppsala, July, September and December 1982.

Profiles E and F, Fig.(8.11), observed in July and September 1982, also exhibit a clear seasonal distribution of ^{18}O in the soil. The snowmelt-contributed ^{18}O -depleted layer moved from average depth 115 cm in July (profile E) to average depth 155 cm in September (profile F). The rate of moisture movement for this period (using eq.8.5) is 6.3 mm/day. The short term or seasonal rates of moisture movement and fluxes are summarized in Table (8.3).

Table (8.3) Rates of soil moisture movement (i.e. the water particle velocity) and moisture fluxes estimated by ^{18}O methods in plot U₂, Uppsala.

Period	Name of profiles	Average position of ^{18}O -depleted moisture layers (cm)	Displacement (cm)	Average soil moisture (vol%)	Rate of moisture movement (mm/d)	Moisture flux (mm/d)
1982						
22 July to 24 Sept	E - F	115 - 155	40	14.6	6.3	0.92
24 Sept to 12 Dec	F - G	155 - 160	5	11.0	0.6	0.07
22 July to 12 Dec	E - G	115 - 160	45	14.6	3.2	0.47
1983						
17 March to 8 June	H - J	40 - 85	45	10.7	5.4	0.58
8 June to 17 Aug	J - K	85 - 140	55	16.3	7.9	1.28
17 March to 17 Aug	H - K	40 - 140	100	13.7	6.5	0.89

It has also been possible to estimate seasonal recharge by tracing the relatively heavy isotope inputs from summer rains. For example, the moisture layer found at average depth 70 cm in December 1982, Fig.(8.11) profile G, has a relatively higher ^{18}O content and is contributed by 1982 summer rains. Between 130 to 190 cm, the ^{18}O -depleted moisture is contributed by 1982 snowmelt and further below there is yet another moisture layer having high ^{18}O . This last layer, average depth 240 cm, is ascribed to the contribution from 1981 summer rains. Thus, we have two summers' contributions at average depths 70 and 240 cm, respectively. The total amount of soil moisture between these layers was 326 mm, which is the percolation or eventual recharge between summer 1981 and 1982, Table (8.2).

^{18}O profiles of soil moisture obtained in March and May 1983 are shown in Fig.(8.12). The sampling in March was restricted to 160 cm only. The ^{18}O -depleted soil moisture present between 20 and 60 cm (average depth 40 cm, profile H) represents the snowmelt of 1983, whereas the presence of the second depleted layer at 140 cm may be ascribed to snowmelt 1982. This second layer's width might have been broader had deeper sampling been

done. In May 1983 the isotopic picture of the soil profile is a bit distorted, at least down to 150 cm, Fig.(8.12). On one hand, the ^{18}O -depleted layer gets very thin (110 to 130 cm, profile I), and on the other, the moisture from 0 to 100 cm depth is highly enriched and bears no resemblance to that observed in March. However, the ^{18}O -depleted layer representing 1982 snowmelt is quite distinct at average depth 200 cm.

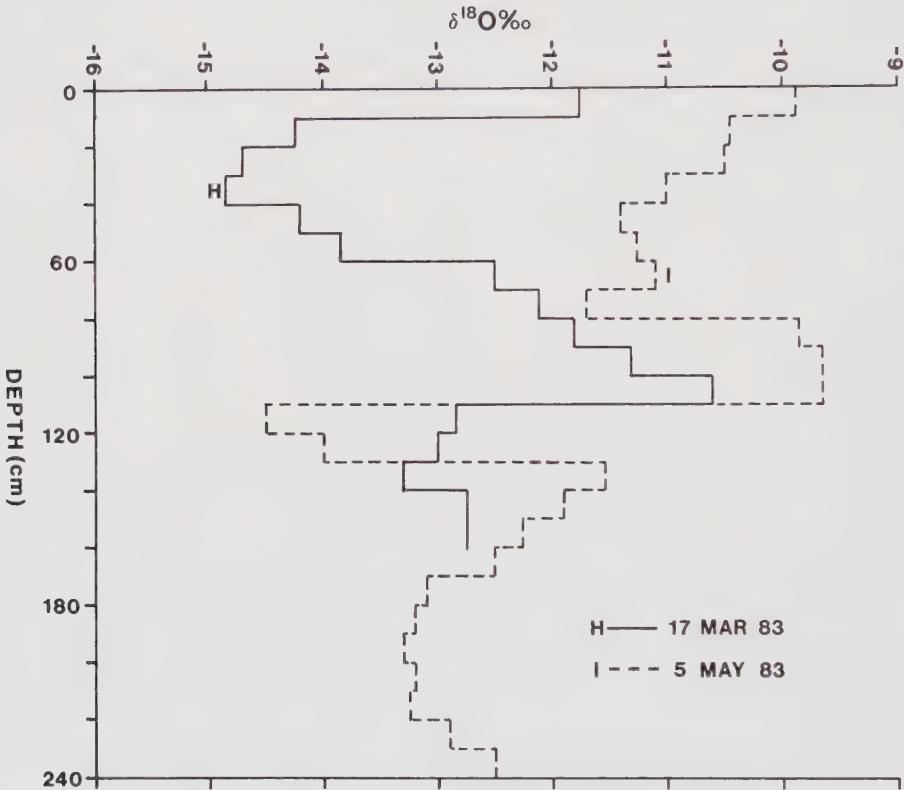


Fig.(8.12) ^{18}O profiles of soil moisture in plot U₂, Uppsala, March and May 1983.

The anomalous behaviour of ^{18}O in 0-150 cm soil depth is difficult to interpret. If one considers that the thin layer of ^{18}O depleted moisture (average depth 120 cm) in May 1983 is due to snowmelt 1983, then the soil moisture between 30 and 80 cm having average $\delta^{18}\text{O} \approx -11.5\text{‰}$ bears no isotopic resemblance to the $\delta^{18}\text{O}$ of precipitation of the post-snowmelt period. The presence of the sharp hump between 80 and 110 cm ($\delta^{18}\text{O} \approx -9.8\text{‰}$) cannot be explained either. Physical inspection of the

desiccator-dried soil revealed the presence of clay, here and there, in the samples from the 80-120 cm zone. It is therefore suspected that the small clay lenses in the shallow depths caused a strong lateral dispersion of soil moisture and distorted the vertical piston flow. In fact, any two soil profiles taken on the same day and 1.5 m apart have shown variations in their ^{18}O and moisture contents. This strongly suggests that field variability of the soil physical parameters is responsible for these deviations. The effect of field variability on δ and moisture values will be illustrated and discussed in the next section.

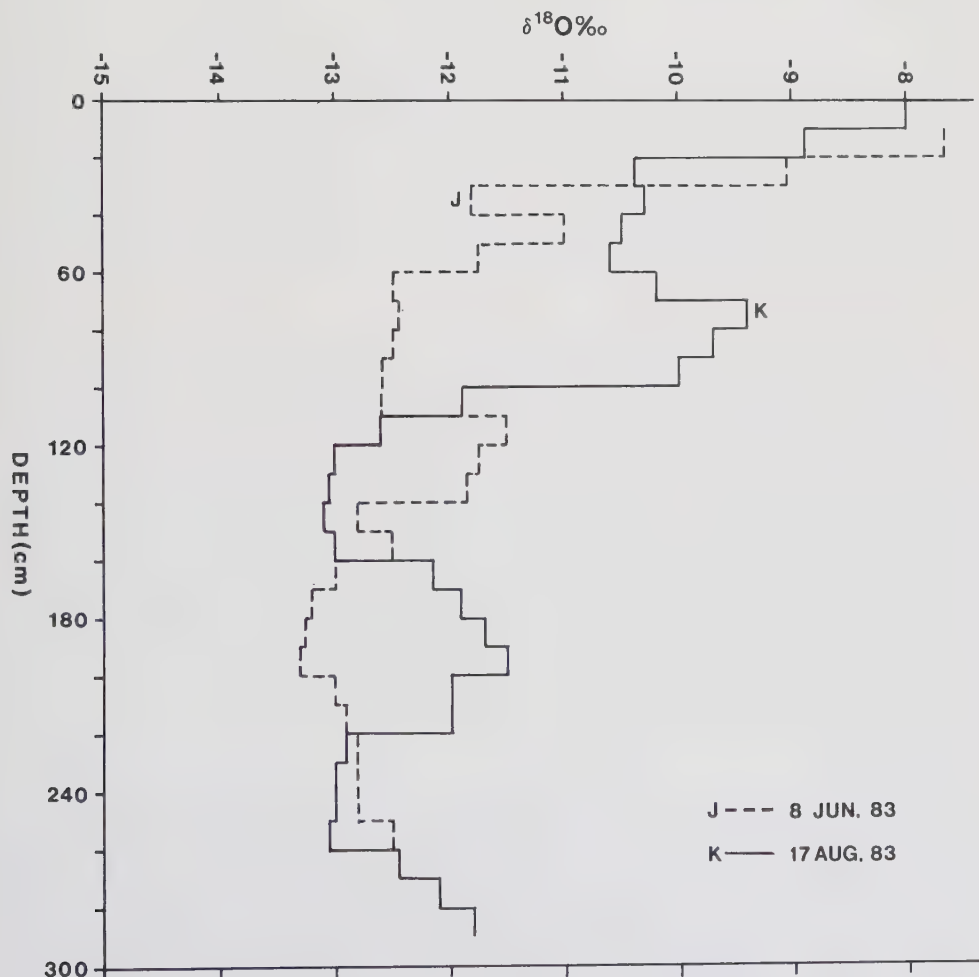


Fig.(8.13) ^{18}O profiles of soil moisture in plot U_2 , Uppsala, June and August 1983.

The ^{18}O profiles observed in June and August 1983 are shown in Fig.(8.13), profiles J and K. The ^{18}O -depleted moisture contributed by 1982 and '83 snowmelt is seen clearly in both profiles, at average depths 85 and 190 cm in June 1983 and at 140 and 240 cm in August 1983, respectively. The percolation between snowmelt 1982 and 1983 obtained from two different profiles observed in June and August 1983 amounts to 189 and 190 mm respectively. These two independent estimates are very similar, Table (8.2), as was also the case during 1981-82 snowmelt (being 280 and 272 mm obtained from May and July samplings). The ^{18}O -depleted layer from 1982 snowmelt was at average depth 70 cm in May 1982 (Fig.8.9, profile C) and is seen at average depth 190 cm in June 1983, having been displaced by 120 cm in this period. The average moisture between these two layers was 18.1%. Thus, the recharge between May 1982 and June 1983 was ≈ 217 mm. Similarly, the corresponding average depths of melt water during July 1982 (Fig.8.11, profile E) and August 1983 (Fig.8.13, profile K) are 115 and 240 cm, respectively. The average volumetric moisture content between 115 and 240 cm was $\approx 20\%$, giving a recharge of ≈ 250 mm during July 1982 to August 1983, Table (8.2).

The annual percolation or eventual recharge between the melt periods of 1981 and 1982 is about 40% of precipitation in this period, being similar to the corresponding value for 1982-83 which is $\approx 43\%$, Table (8.2). From the above study, the annual recharge estimated from the displacement of ^{18}O -depleted or enriched moisture varies from 200 to 330 mm. The mean annual precipitation for the Uppsala region is ≈ 700 mm. The mean annual loss from evapotranspiration estimated by Eriksson (1980) is about 400-450 mm, giving mean annual recharge between 250 and 300 mm, which is in good agreement with recharge estimates obtained from the ^{18}O method.

Kloten

The above methodology of soil sampling was standardized in the sandy (esker) deposits at Uppsala. As the method proved to be quite successful, it was tried in the glacial till at Kloten. As explained earlier, moraine is not amenable to the soil coring method because of small stones and boulders. Hence a pit (190 x 80 cm) was dug to a depth of 2 m at Kloten. Soil samples were collected at 10 cm interval from the walls of the pit in September 1983. The ^{18}O profiles of two walls of the pit are

shown in Fig.(8.14). A big boulder found at one wall prevented the sampling below 1 m depth.

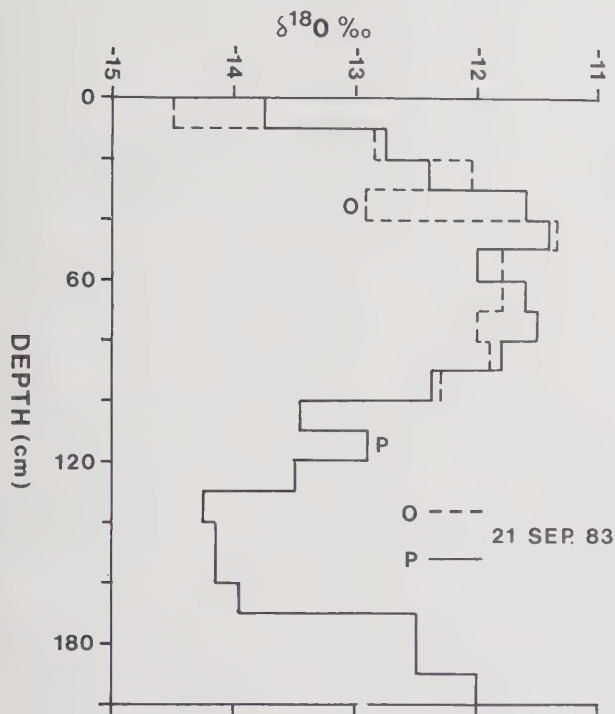


Fig.(8.14) ^{18}O profiles of soil moisture in Kloten, September 1983.

Except the sharp difference between ^{18}O content at one depth (30-40 cm), the other minor variations are due to field variability. The presence of ^{18}O -depleted layer at average depth 150 cm (profile P) is contributed by the spring melt of 1983. Assuming that at the end of the melt period this depleted layer was approximately at average depth 40 cm (taking an analogy with Uppsala) in March 1983, then it was displaced 110 cm until the end of September 1983. The rate of soil moisture movement for the above period is ≈ 5.8 mm/d, Table (8.2). The profile (P) is well defined and the ^{18}O -depleted or enriched moisture is easily identified. The average depth of enriched moisture from 1983 summer rains is at 60 cm, Fig.(8.14). Extrapolating profile (P) and assuming that the average depth of the enriched moisture contributed by 1982 summer is at 220 cm, then the annual recharge in Kloten was about 266 mm between summer 1982 and 1983. The average moisture content between 60 and 220 cm was 16.6%. It is thus concluded that the method could be applied in moraine formations also, despite the cumbersome procedure of pit digging. Had it been possible to sample deeper, ^{18}O -depleted moisture from 1982 spring melt might have been detected also.

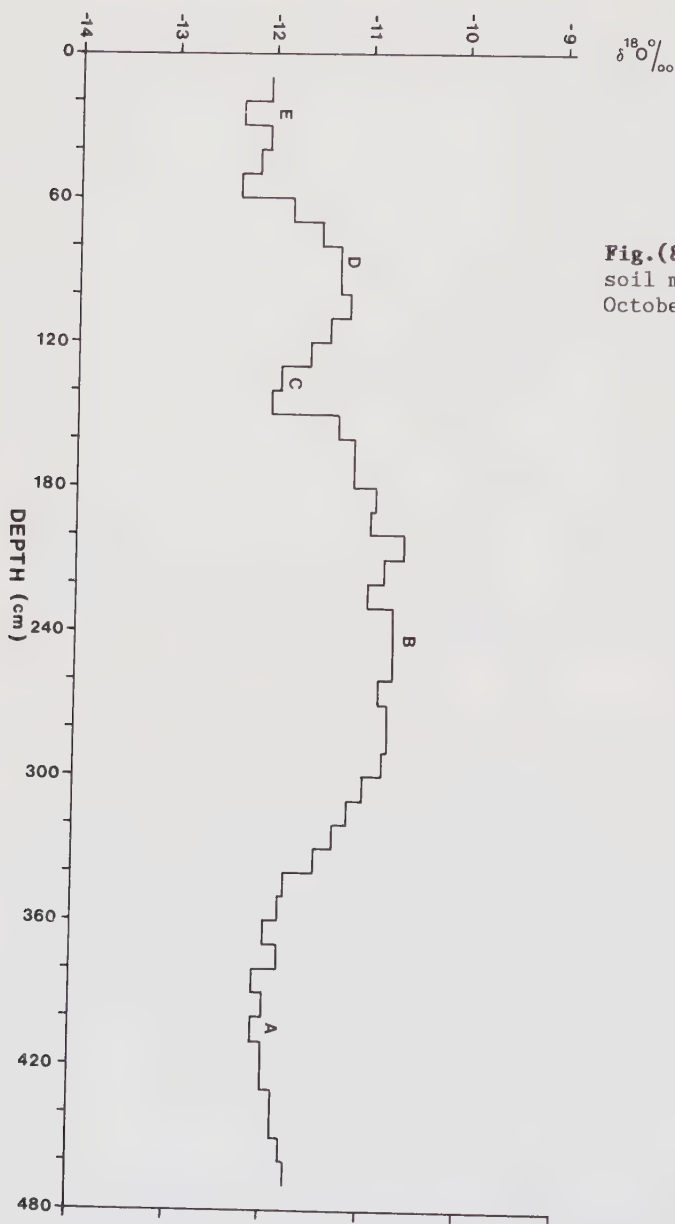


Fig.(8.15) ^{18}O profile of soil moisture in Örbyhus, October 1984. Profile R.

Örbyhus

Another moraine formation was studied in October 1984 on a small ridge at Örbyhus. A mechanized pit digging machine was used to make a 6 x 6 m pit to a depth of 4.75 m. The ^{18}O profiles of soil moisture taken at 2 points 5 m apart are shown in Figs (8.15) and (8.16). The profiles have a field variability

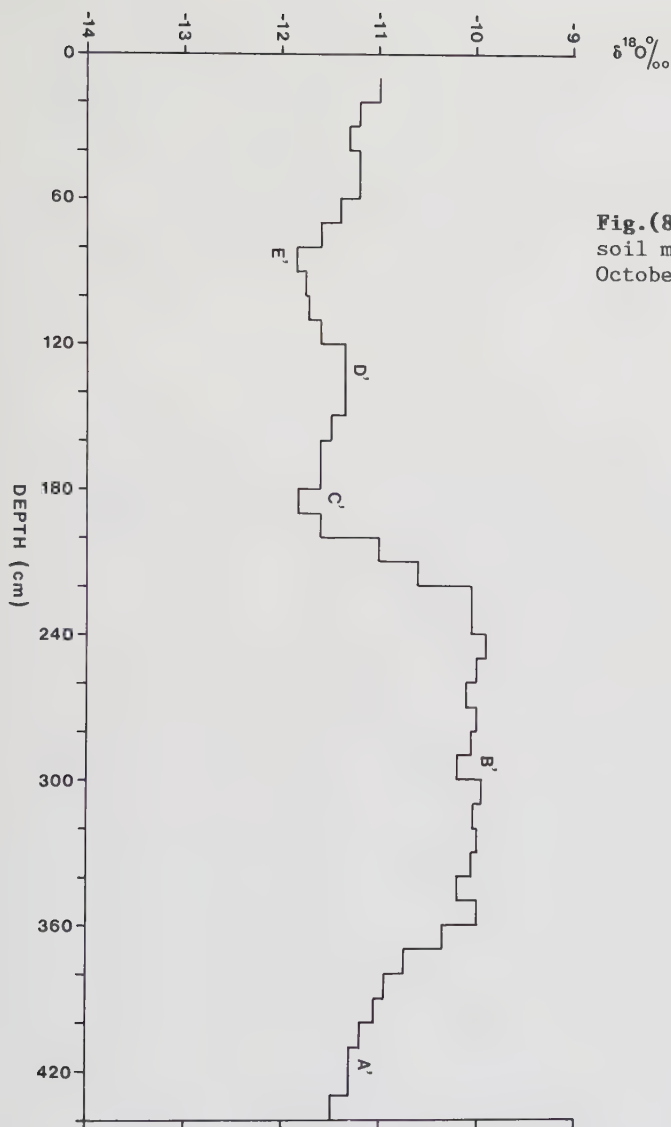


Fig.(8.16) ^{18}O profile of soil moisture in Örbyhus, October 1984. Profile Q.

specially between 60 and 200 cm, but deeper below they have almost a similar character. Relatively, profile R, Fig.(8.15), is rather complete, where contributions from spring 1983 (point A), summer 1983 (point B), spring 1984 (point C), summer 1984 (point D) and autumn 1984 (point E) are easily discerned. In profile R, the average position of the ^{18}O -depleted moisture from snowmelt 1983 is 400 cm, and the average position of 1984 snowmelt is 140 cm; therefore the recharge during this period is 260 mm, the average moisture content being 10% (vol.) in the

layers (140-400 cm). Almost similar recharge is obtained from profile Q, Fig.(8.16), considering that the average position of ^{18}O depleted moisture from 1983 snowmelt is 440 cm and that of 1984 is 180 cm. The relatively higher δ values of the spring 1983 and 1984 are due to higher δ values in precipitation during that period. These conclusions are rather rough as Uppsala precipitation data have been used for Örbyhus as well. The validity of such a similarity in precipitations is quite questionable, but for a rough estimate one can assume isotopic composition of precipitation to be almost the same for both locations.

8.9 Field variability of ^{18}O in soil moisture

The soils in the glacio-fluvial deposits in Uppsala and the glacial till of Kloten and Örbyhus are in no way homogeneous. In heterogeneous soils, it has been found that the soil physical properties, i.e. hydraulic conductivity, varies from point to point and the moisture flux differs from profile to profile, Dagan and Bresler (1979). The mass transfer of water in such soils is by transport through the pores and by hydrodynamic dispersion or diffusion. While the mean pore velocity of water in the soils has a well defined meaning, the contribution of diffusion to the transport of fluids in the unsaturated soils is difficult to measure, specially when they are heterogeneous. The heterogeneity of soils yields different rates of soil moisture movement from point to point in the same location. Soil samplings at Uppsala, Kloten and Örbyhus have shown that $\delta^{18}\text{O}$ profiles of the soil moisture taken 1 to 4 m apart vary by $\approx 1\text{‰}$ at the maximum in their δ values. The relative variation has been random, i.e. sometimes small and sometimes rather large. In August 1983, three sampling points about 1 to 3 m apart were sampled to obtain $\delta^{18}\text{O}$ profiles of soil moisture. The three $\delta^{18}\text{O}$ profiles are shown in Fig.(8.17). It is immediately seen that the profiles are somewhat different relative to one another though similar in the general trend. As expected, the soil moisture content was also different for these profiles. It may be pointed out at this stage that these three sampling points were deliberately chosen to represent extreme heterogeneity with respect to the appearance of the soil surface. While one point was on a flat patch, the other was on a small hump and the last one in a small depression. These three features are typical of a gently undulating but otherwise flat landscape. Field variability in $\delta^{18}\text{O}$ profiles is illustrated in Kloten moraines Fig.(8.14) and in those at Örbyhus, Figs (8.15)

and (8.16). At Kloten the profiles are very much alike, except between 30 and 40 cm, whereas Örbyhus shows considerable differences in δ values as well as the average positions of the ^{18}O -depleted and enriched layers. The extreme δ value difference in Örbyhus profiles is about 1.5‰ and the same is also observed in Uppsala in August 1983 as well as in July-September 1982 in plots U_1 and U_2 . It is therefore quite clear that several profiles of ^{18}O should be obtained to improve the accuracy of estimates.



Fig.(8.17) ^{18}O profiles of soil moisture in Uppsala observed on the same day. Sampling points being 1 to 1.5 m apart from one another.

8.10 Conclusions

The use of the stable isotope ^{18}O for the measurement of soil moisture movement and the estimation of groundwater recharge seems to be quite promising. The chief advantage over other methods is that for those regions where the water table is deep enough, a single ^{18}O profile of soil moisture is sufficient to locate two consecutive years' summer rain or snow meltwater in the soil giving a direct measure of yearly percolation or recharge. The rate of soil moisture movement can be determined from the temporal displacement of ^{18}O depleted or enriched soil moisture layers in the unsaturated zone. The ^{18}O method is free from radiation hazards, does not contaminate the environment and the ecology is preserved. The H_2^{18}O molecule has the same chemical properties as H_2^{16}O , thus the problems of retardation and adsorption into the soil matrix do not arise.

The ^{18}O tracer technique makes it possible to trace the movement of water and follow its pathways which can be used to study the problem of acidification and increased leaching of nutrients in the groundwater where proper knowledge of water flowpaths is needed. When chemical processes are involved, the ^{18}O tracing can determine the residence time of water particles in different soil zones and the origin of recharging water.

The above method is useful for a country like Sweden, because the large seasonal isotopic difference in the precipitation offers a natural tagging of soil moisture.

9 FRACTIONATION IN THE UNSATURATED ZONE

9.1 Fractionation due to evapotranspiration from soils

While dealing with moisture movement in the unsaturated zone, it is important to investigate the isotopic fractionation that occurs just after water infiltrates in the soil profile. After infiltration in the soil, the soil moisture is subject to evaporation in bare soils and evapotranspiration in vegetated soils.

Zimmermann et al. (1967a) studied the effect of transpiration in a rather simple laboratory experiment. They planted saplings of various plant species in glass bottles filled with water of known isotopic content. The necks of the bottles were plugged with wax to avoid contact between water in the bottles and the atmosphere, and when about 50% of the water in the bottles was consumed by plant transpiration, the remaining water was checked for its isotopic content. They found that the water in the bottles had the same isotopic composition as in the beginning and concluded that pure transpiration from soils is non-fractionating in nature. The above experiment rather closely simulated transpiration from a saturated soil.

Allison et al. (1984) in laboratory experiments studied the fractionation of soil moisture by transpiration, simulating semi-arid conditions. Wheat and sunflower were grown in a sandy material with little organic matter. When the plants had developed from the germination stage to about 200 mm in height, a nutrient solution of known isotopic content was flushed through the pots. The pots were then sealed by a soft hydrocarbon wax layer, applied at the surface and at the drainage holes in the bottom. The plants were allowed to grow for four weeks until the available soil moisture was consumed. The remaining moisture in the pots was then analysed for ^{18}O and D. It was observed that the D content of soil moisture decreased by about 8‰ while ^{18}O increased by about 1‰. These changes in the isotopic composition of remaining soil moisture were attributed to a 25% breakdown of the organic material in the root zone to water and CO_2 . No conclusive proof of fractionation by transpiration was found.

Allison et al. (1984) also suggested that the decomposition of organic material under very dry soil conditions may modify the

isotopic composition of soil water. They also cautioned that plant species adapted to arid conditions would extract water from the soil at very high suctions, inducing vapour transport to their roots, which would bring about fractionation of remaining soil moisture.

Transpiration can be compared to suction of moisture through capillaries extending from the roots to the leaves of a plant. Every small parcel of water sucked up to the leaves arrives without suffering fractionation. The basic assumption being that roots have no preference to isotopically lighter water. Evaporation at the leaf surface may bring about some fractionation but the next incoming parcel of water pumps out the previous one. There may be a slight mixing among these parcels but the capillary resistance is too great to allow any influence on the soil moisture. The leaf as such may be slightly enriched relative to soil moisture.

In another experiment, Zimmermann et al. (1967a) measured enrichment of soil moisture during evaporation in controlled laboratory conditions. Soil columns of sand were allowed to evaporate under constant humidity and the water table was kept near to the soil surface. After a certain span of time the soil columns were sliced into thin portions and analysed for their deuterium content. It was found that the deuterium content was highest near the soil surface and decreased exponentially with depth. This is illustrated schematically in Fig.(9.1). The mean penetration depth of the enrichment front was inversely proportional to the evaporation rate at steady state conditions.

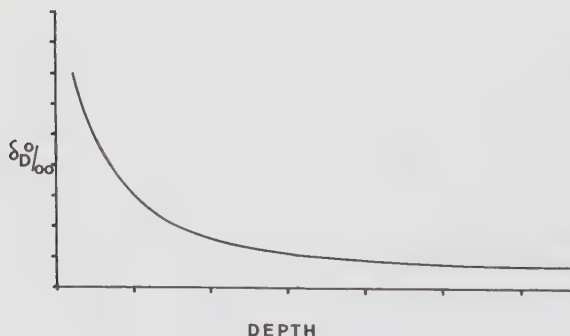


Fig.(9.1) Schematic δD distribution of soil moisture in a laboratory soil column. Water table being just below the soil surface (saturated soil).

From the above they concluded that for central European climates, due to the interplay of the evaporation rate, the mean penetration depth and probable length of dry intervals between

two consecutive rainfalls, the average enrichment in bare-soil moisture would be about 10‰ in D and 1‰ in ^{18}O . Therefore, one cannot expect a large average enrichment even in summer because of the mean penetration depth of enriched moisture being too small. Barnes et al. (1983) theoretically discussed the enrichment in dry soils, and based on this work Allison et al. (1983) studied the depth distributions of ^{18}O and D of soil moisture in columns undergoing steady and quasi-steady evaporation. They found that under steady-state and isothermal conditions in relatively dry soils (water table being well below the soil surface), the isotopic concentration rises from a low value at the soil surface to a maximum in the region where the liquid transport of moisture dominates, schematically shown in Fig.(9.2). Below the vapour-liquid boundary, the concentration falls off exponentially, the form of the profile below the maximum being similar to that observed by Zimmermann et al. (1967b) who had the water table very near the surface of the columns.

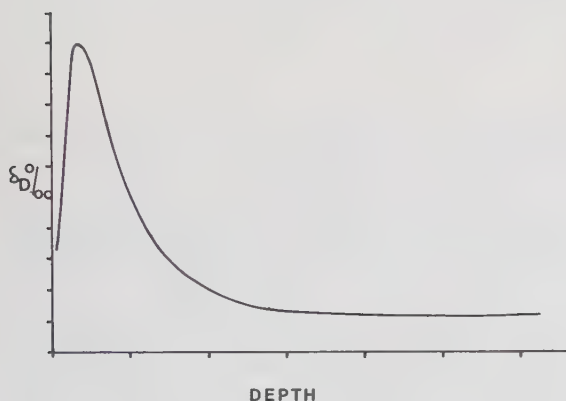


Fig.(9.2) Schematic δD distribution of soil moisture in a laboratory soil column. Water table being well below the soil surface (unsaturated soil).

Münnich et al. (1980) have also discussed the isotope fractionation from laboratory sand columns (unsaturated soils) and their experimental results are similar to those observed by Allison et al. (1983). Allison et al. (1984) have further discussed the possibility to separate evaporation from the total evapotranspiration flux by determining the thickness of the dry surface layer using isotope profiles. They also developed a simple conceptual model which predicts that the isotopic composition of soil moisture at a certain depth is shifted from the meteoric line by an amount proportional to $1/\sqrt{R}$ where R is the local recharge. The model is an oversimplification of the natural process, i.e., it is assumed therein that all the rainfall

events are of equal amounts and occur after constant intervals of time. The isotopic shift of the soil moisture from the meteoric line being proportional to $1/\sqrt{R}$ could not be confirmed experimentally because of the paucity of data. Münnich et al. (1980) and Allison (1982) found in laboratory soil columns that in evaporation from relatively dry soil columns where vapour transport is dominant, the ^{18}O -D slope of soil moisture is lower relative to wet soils where liquid transport is a dominating factor. In desert sands, Dinger et al. (1974) found that the ^{18}O -D slope was ≈ 2.0 against the usual value 5.0 found for open water bodies subject to evaporation.

From the above laboratory and field studies, it is inferred that in arid conditions the isotopic composition of soil moisture is largely influenced by isotope fractionation due to evaporation, specially from the region where vapour-phase transport dominates in the soil profile. However, for European conditions the effects of fractionation on soil moisture by evaporation are expected to be low. In Swedish conditions it is interesting to investigate the extent to which the isotopic content of soil moisture will change due to evaporation from bare or vegetated soils.

9.2 Fractionation in lysimeter percolates in bare soil

In order to investigate the overall fractionation of soil moisture (in Swedish climatic conditions) which eventually mixes with the groundwater, a lysimeter study was undertaken in 1981-82 in Uppsala during the summer months. The diameter of the lysimeters was 50 cm and they were filled with fine sand in one, medium-fine or coarse sand in the second and gravel in the third. The depth of the filling was about 1 m, the total depth of the lysimeters was about 1.1 m. The lysimeter percolate was collected in plastic bottles attached to the outlet of the lysimeters. The lysimeters were covered on the top and sides by a thin sheet of polythene in the form of a tent to shield them from rain, but allowed a free flow of air from the sides.

Prior to the beginning of the experiment, the lysimeters were irrigated with 40 litres water ($\delta^{18}\text{O} = -11.7\text{‰}$) and allowed to drain. A week later, the percolate was analysed for ^{18}O content which was roughly the same as that of input water. The lysimeters were again irrigated with 15 litres water having the same δ value, and the percolate was collected at weekly/biweekly

intervals. The δ values of percolate (summer 1981) are plotted against time in Fig.(9.3). The δ value of irrigation water is shown as square blocks.

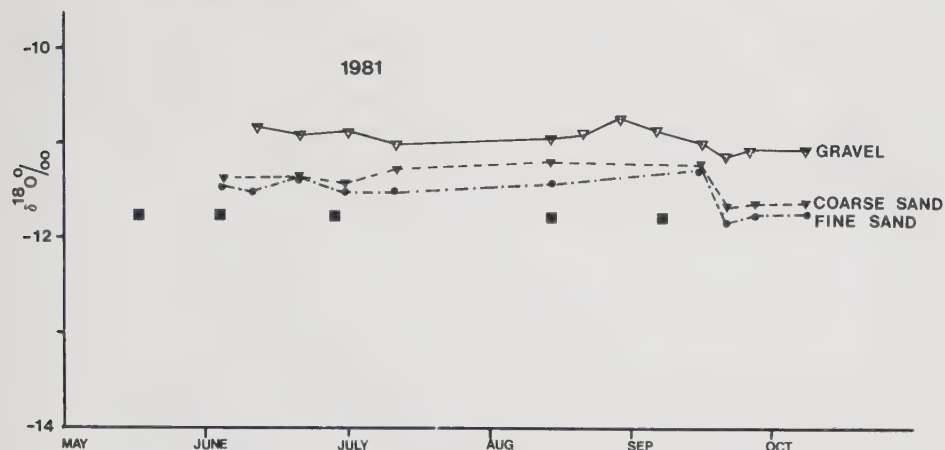


Fig.(9.3) $\delta^{18}\text{O}$ of leachate from lysimeters in Uppsala 1981. Square blocks denote the δ value of irrigation water.

It is seen from Fig.(9.3) that the percolates from fine and coarse sand are enriched to a minor degree in ^{18}O content relative to irrigation water, whereas the percolate from gravel material is considerably enriched. In other words, isotopic fractionation of soil moisture seems to be more pronounced in coarse rather than fine material.

Münnich et al. (1980) observed higher enrichment of soil moisture in coarse sand than in fine sand, which could not be predicted by their simple fractionation model. They drew a parallel between the high enrichment in coarse material to the kinetic fractionation in evaporation from a free water surface. They proposed that dry air having greater density than moist air may cause sinking of dry air at one place and rising of moist air at another in the vapour diffusion zone in the soil. This convective transport of water vapour may not be necessarily fractionating but adds to the diffusive transport, thus increasing the mean penetration depth of the enrichment front.

The above experiment was repeated in summer 1982, Fig.(9.4). It was again observed that the percolates were enriched relative to the ^{18}O of the irrigation water, the fine-grained soil showing little enrichment and the coarser-grained showing

higher enrichment. Compared to summer 1981, the δ values in the percolates during 1982 from fine and medium grained soil are very much alike, apart from showing a big difference in $\delta^{18}\text{O}$ content on one occasion, Fig.(9.4). This difference is attributed to a possible measurement error. The percolate from gravel showed higher enrichment as was the case in 1981 also. In general, the data from 1981 and 1982 show that from fine and medium sand the enrichment of soil moisture is about 0.2 to 0.7‰ while in the coarse material, i.e. gravel, the enrichment is rather high, varying between 0.7 and 1.2‰.

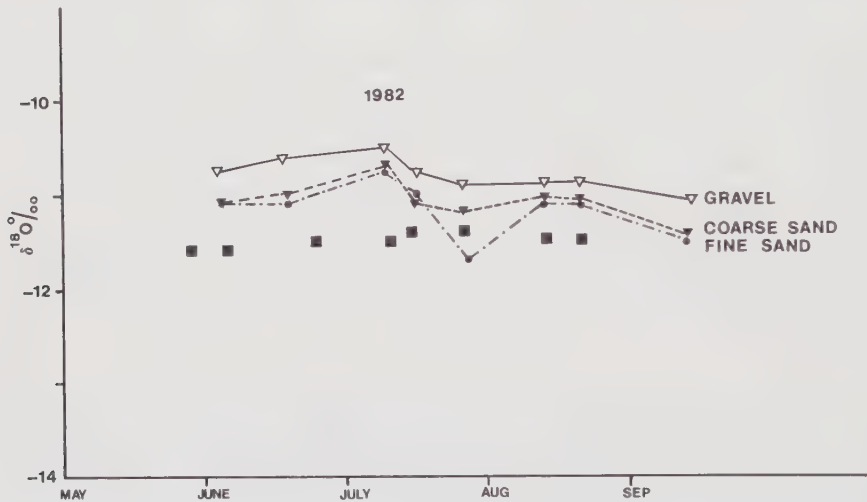


Fig.(9.4) $\delta^{18}\text{O}$ of leachate from lysimeters in Uppsala 1982. Square blocks denote the δ value of irrigation water.

The δ value of the percolates decreased a little around September in both years. This is due to the onset of a relatively cooler period during which evaporation from the soil surface was quite reduced. Consequently the enrichment was also less.

9.3 Conclusions

The above observations are valid for bare soils only during the summer period. In vegetated soils the fractionation will be relatively less than in bare soils, because transpiration will remove the bulk of the soil moisture and this process is considered to be nonfractionating.

For Swedish till soils, the enrichment of soil moisture during summers is expected to follow the pattern of fine and medium coarse sand. Thus less than 1°/∞ enrichment of soil moisture may be encountered which is about the same as assumed by Zimmermann et al. (1967a).

10 SEASONAL FLUCTUATIONS OF OXYGEN-18 IN GROUNDWATER IN FISSURED ROCK

10.1 Introduction

The characteristics and origin of groundwaters have been successfully studied using the variations in the abundance of stable isotopes (^{18}O and D) of the water molecules. This has been possible due to the conservative nature of the stable isotopes in an aquifer provided water is not subjected to temperatures above 60-80°C. When aquifer temperatures are above 80°C, a rapid change in the isotopic composition of groundwater occurs and its composition changes drastically relative to its previous or original value. Clayton and Steiner (1975) have observed that at high temperatures occurring in geothermal fields, the ^{18}O content of water increases while that of the rock decreases. The isotopic changes in oxygen are much higher than hydrogen as the hydrogen content of rocks is far too low to significantly affect the D content of geothermal waters.

In non-geothermal systems, generally the isotopic composition of the meteoric groundwaters is found to "match" the annual mean composition of precipitation over the recharge area. However, this isotopic "match" between the groundwater and the local precipitation is not perfect. Suffice to say that very often groundwaters "remember" the isotopic composition of their origin. The changes in the isotopic composition of groundwater are mainly a function of the recharge processes. In humid regions, the infiltrating precipitation will not suffer considerable enrichment, as direct evaporation from the soil is low, the transpiration is nonfractionating and the groundwater will more or less reflect the isotopic composition of precipitation. In arids and semi-arids where the vegetative cover is sparse and evaporation from bare soils considerable, the groundwaters have been found to be slightly enriched relative to local precipitation, Gat (1974). The opposite effect, i.e. a depletion in the isotopic content of groundwaters, in some arid regions in Africa have been reported by Vogel and Van Urk (1975) and in other desert areas by Levin et al. (1980). The observed depletions can be explained by the selective events of recharge, i.e. small amounts of precipitation of generally high δ values are lost by evapotranspiration while large showers of lower δ values percolate through the unsaturated zone and eventually mix with the groundwater system.

10.2 Seasonal variations of ^{18}O in groundwater in fissured rock at Finnsjön

To study the impact of seasonal variations of ^{18}O in precipitation on the ^{18}O content of groundwater, a field study was initiated in the fissured rocks at Finnsjön in 1982.

The yearly weighted mean $\delta^{18}\text{O}$ of precipitation observed at a gauging station, Hedesunda, in the neighbourhood of Finnsjön is -12.1‰ ; Burgman et al. (1983). Groundwater δ values observed at 260, 382 and 494 m depths were -11.0 , -11.8 and -12.1‰ respectively, corroborating the view that meteoric groundwaters are isotopically similar to local precipitation. However, preliminary isotopic observations at "shallow depths" (10 to 90 m) showed strong seasonal fluctuations, leading to the present investigations.

Finnsjön has earlier been a test area to explore the possibilities of storing high level nuclear waste in crystalline rock. Hydrogeological investigations for this purpose have been carried out in this area earlier; Carlsson and Gidlund (1983). The area has several boreholes penetrating to 100 m while some have been drilled to more than 500 m depth.

10.3 Site description

Finnsjön is situated 100 km north of Stockholm and 16 km southwest of Forsmark nuclear power plant. Finnsjön is 25 km^2 large in area with generally a flat topography, characterised by the subcambrian peneplane formed more than 570 million years ago. The highest and the lowest points in the area are about 40 and 18 m above mean sea level respectively. The bedrock is a mixture of different rock types occurring within the Sveco-Fennian area in Sweden. The area is dominated by granodiorite but other rock types, i.e. leptite, granite, metabasite, pegmatite and aplite, are also present. The rock system often occurs as bare out-crops, but generally is covered by a thin cover of fluvial till and about 10% of the area is covered by clay, sand, silt and gravel. The thickness of the soil cover is small, the till is at most a couple of meters thick, but the most frequent thickness is about 1 m. Clay occurs in topographical low points and extends to about 5 m in depth. Seven deep boreholes (500-700 m deep) and sixteen boreholes (100 m deep) have been made by core drilling and percussion method respectively. The inner diameter of the boreholes is 115 mm. The depth to the water

table in this area varies from 4 to 7.5 m in the recharge zones while water logging is generally encountered during snowmelt and other wet periods in the discharge zone.

The exposed bed-rock has been studied for fractures, the fracture frequency is 3.0 fractures per meter on the average. The fracture frequency measured on the drill cores is about 2.5 fractures per meter. No tendency of decreasing fractures with increasing depth was observed. The average annual precipitation in the area is about 670 mm, while the annual run-off is 240 mm approximately.

10.4 Experimental procedure

Hydraulic conductivity of all the boreholes has already been determined by water injection tests at constant head, Gustafsson and Klockars (1981). Only those sections of the boreholes which had a relatively high hydraulic conductivity (10^{-7} to 10^{-4} m/sec) were chosen as sampling depths for groundwater samples. Water samples from these depths were taken periodically, at one month's interval or more depending upon the field logistics. Groundwater sampling of the boreholes was started in December 1981.

The water sampler (50 mm diameter) is designed to close at a desired depth by a messenger (a cylindrical metal weight) which slides down the cable, hits the spring-loaded top section of the sampler, which closes the water sampler at the top and the bottom. About 150ml water is collected at a time.

The ^{18}O of the water samples was measured by ratio type mass spectrometer in the manner described earlier. Electrical conductivity was measured at 20°C by a digital conductivity meter and is expressed in $\mu\text{S}/\text{cm}$. The water temperature at the desired depths was measured by a thermometer attached to the inside of the supporting rod of the water sampler. The temperature measurements are accurate to 0.1°C .

10.5 Comparison of sampling methods

In order to check whether standing water in the borehole section represents the incoming water from the fissures present in the section and not the old water, which is continuously affected by vertical currents in the borehole, different methods of sampling were adopted and compared with the usual sampler method. These

are electrical pumping by a centrifugal pump and pressure pumping by compressed dry nitrogen. The section of interest in a borehole was isolated by inflating packers against the borehole walls. The section in between the packers was pumped by the centrifugal pump and sometimes by pressure pumping. The electrical conductivity of the pumped water was continuously recorded at the site. It was observed that when about three section volumes were pumped out, the electrical conductivity reached a constant value. This stage of constant electrical conductivity represents the water coming from the borehole section, which is fed by the fissures and cracks present in it. Water entering the pumping tube during its lowering in the borehole is thus already replaced by the water from the desired depth.

The water collected at certain depths by the water sampler and the water collected by electrical and pressure pumping after flushing out three section volumes are compared against one another in terms of their ^{18}O content. In those boreholes where the hydraulic conductivity is relatively low, the isolated depth was pumped through a narrow plastic tube. Pumping by compressed nitrogen was a slow process as the section took some time to fill up with water. Narrow tubes were used in order to quicken the process of flushing out the tube filled water during the lowering of the assembly in the borehole. A total of three boreholes were investigated to obtain a comparison between the usual method of sampling by the water sampler and electrical and pressure pumping.

A comparison between the $\delta^{18}\text{O}$ of water from some depths, as observed by the usual sampling method and by the pumping tests at the same depths but using packers is shown in Table (10.1). Borehole G3, which has a very high yield, was subjected to electrical pumping while G7 and G9 were sampled by pressure pumping using compressed nitrogen. The depths in question were isolated one at a time, the length of isolated section was 1.7 m in case of electrical pumping and 1.95 m in case of pressure pumping.

It is observed that the ^{18}O content of samples taken by the water sampler and by the pumping method was the same. This implies that water sampled at a particular depth represents that water which is coming from the neighbouring fissures and is not affected by vertical mixing within the borehole.

Table (10.1) A comparison between the $\delta^{18}\text{O}$ of water sampled from the boreholes by the water sampler and by pumping.

Bore-hole	Depth (m)	Date	$\delta^{18}\text{O}$ of water sampled:			
			by water sampler	after pumping of 50 l	100 l	water volume 200 l
G3	5.0	83-10-07	-10.8			
	10.0	"	-11.4	-11.8	-11.7	
	25.0	"	-12.0	-12.2	-12.2	-12.1
	65.0	"	-12.0	-11.8	-11.9	
G7	6.0	83-11-03	- 9.4			
	10.0	"	-10.2	-10.2	-10.2	-10.3
	75.0	83-11-09	-10.3	-10.4	-10.4	-10.5
G9	0.6	83-11-14	-12.5			
	10.0	"	-12.5	-12.5	-12.5	-12.4
	50.0	83-11-16	-12.4	-12.3	-12.5	-12.5

10.6 Results and discussions

The electrical conductivity and $\delta^{18}\text{O}$ content of groundwater sampled at different depths of the boreholes, plotted against time are shown in Figs (10.1) to (10.4). It is observed that in all the boreholes except G9, Fig.(10.4), the $\delta^{18}\text{O}$ content at the water table (referred to as surface in the figures) shows a big amplitude of fluctuation, especially after the snowmelt period. The $\delta^{18}\text{O}$ content decreased by 1 to 2‰ between February and April 1982. This big change is due to a direct mixing of snow-melt water ($\delta^{18}\text{O} = -18.6\text{‰}$) with shallow groundwater ($\delta^{18}\text{O} = -12.0\text{‰}$), causing a decrease in its $\delta^{18}\text{O}$. This pattern is repeated at greater depths also, though on a reduced scale.

During April, May and June 1982, groundwater had a minimum $\delta^{18}\text{O}$ value but it began to increase after June because of enriched surface inputs coming from summer rains, which are heavier in $\delta^{18}\text{O}$ content. The $\delta^{18}\text{O}$ of groundwater reached a maximum in November-December 1982 and then again went to a minimum in April 1983, i.e. just after the snowmelt was complete. Compared to 1982, the summer of 1983 was very dry and even the snow cover in March was much thinner than that of 1982. Consequently, after the snowmelt, the magnitude of variation of $\delta^{18}\text{O}$ in 1983 was smaller in comparison to that of 1982, but the trend was similar.

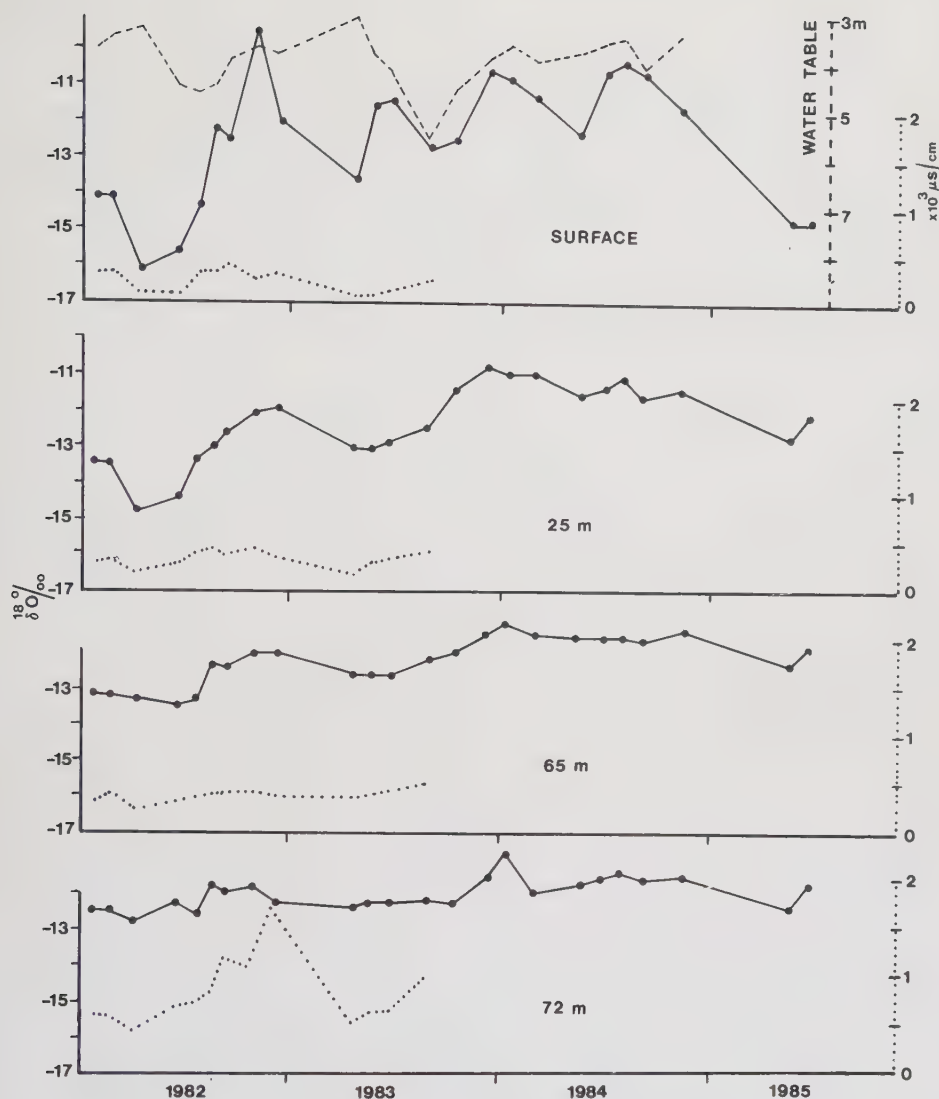


Fig.(10.1) $\delta^{18}O$ (full line), water table (dashed line) and electrical conductivity (dotted line) of groundwater in bore-hole G3, Finnsjön.

This implies that the surface inputs from rain or snowmelt percolate quickly through the fissures in the rock and mix with groundwater. The rather fast percolation and mixing is probably due to the fact that often the rocks are bare at the surface and in some areas have a very thin soil cover.

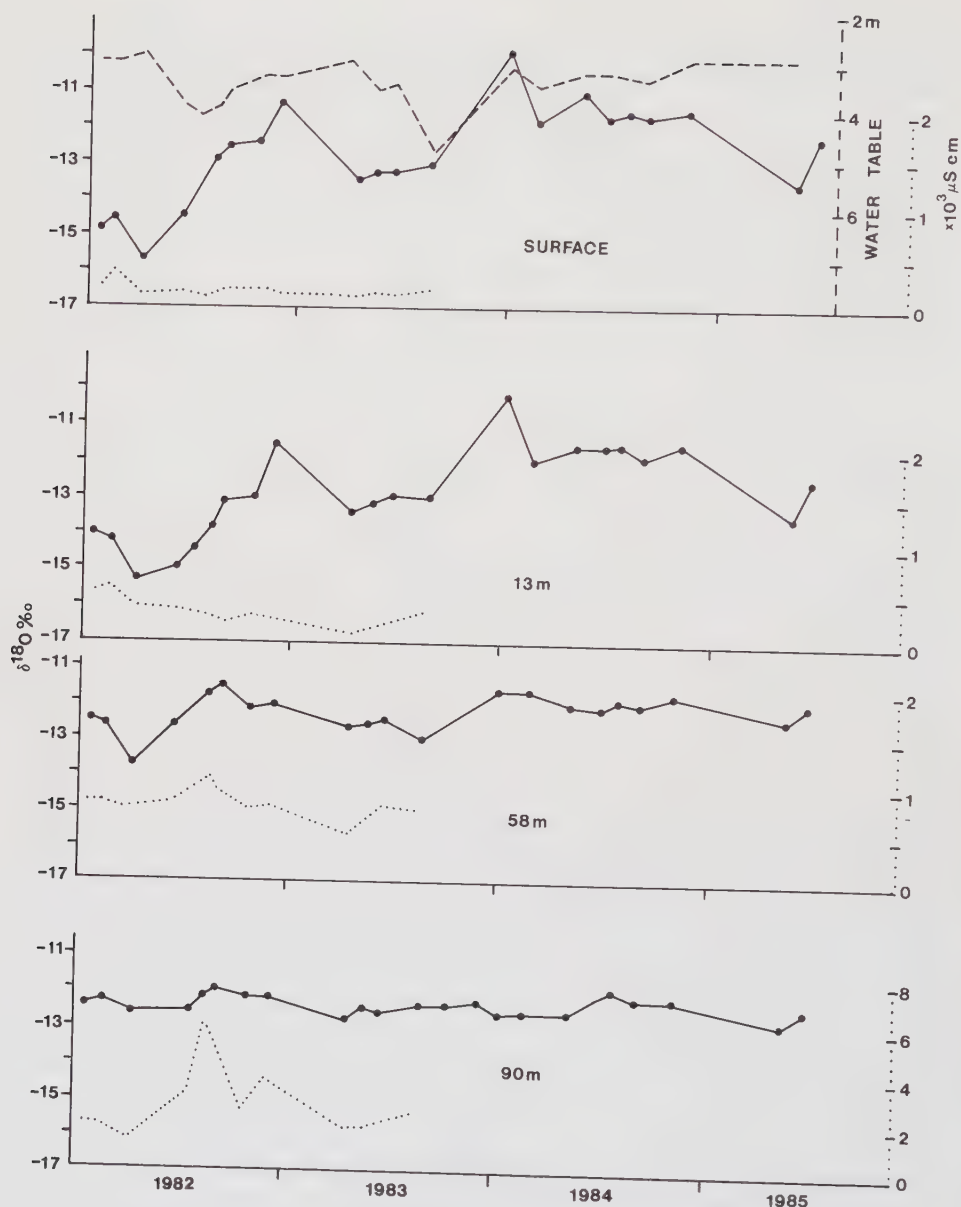


Fig.(10.2) $\delta^{18}\text{O}$ (full line), water table (dashed line) and electrical conductivity (dotted line) of groundwater in bore-hole G5, Finnsjön.

Water table fluctuations and electrical conductivity measurements also support this view. During snowmelt, as the meltwater inputs reach the groundwater, the water table rises, the ^{18}O of groundwater decreases and electrical conductivity also

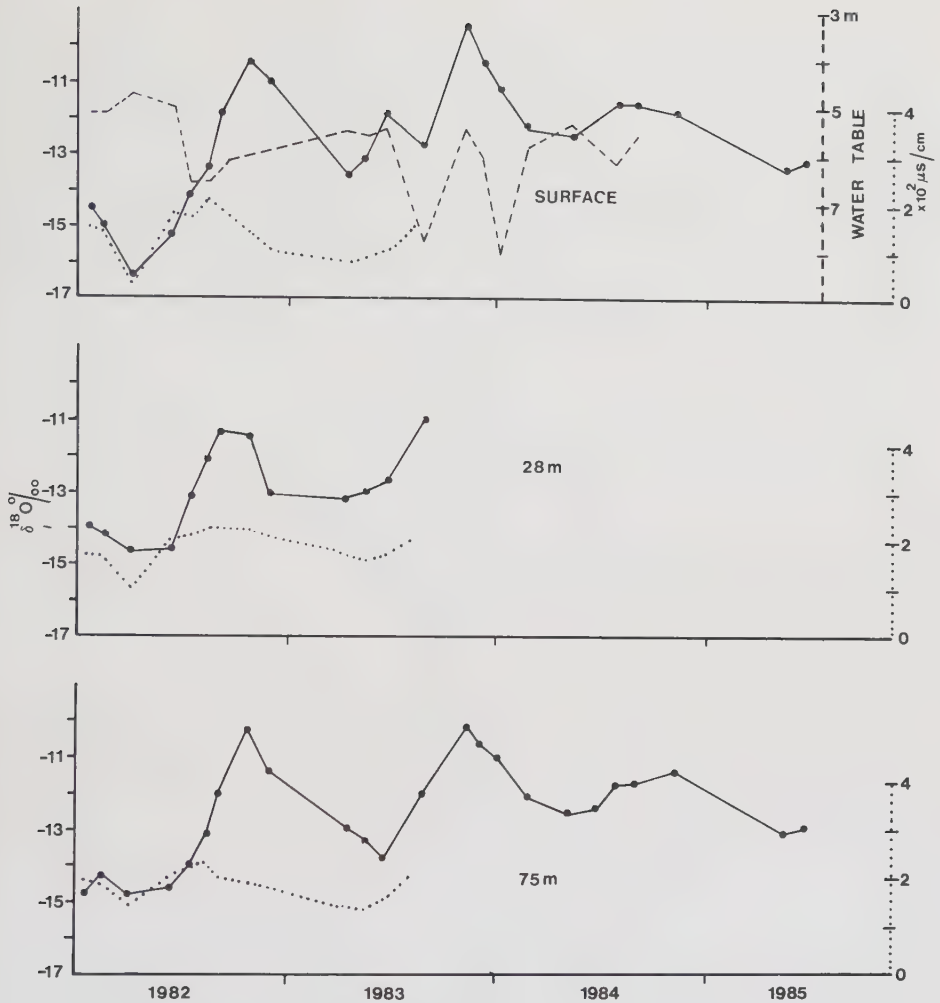


Fig.(10.3) $\delta^{18}\text{O}$ (full line), water table (dashed line) and electrical conductivity (dotted line) of groundwater in borehole G7, Finnsjön.

decreases. During relatively dry periods, the water table is lowered and electrical conductivity increases. These changes remain generally in phase with one another.

Boreholes G3, G5 and G7, Figs (10.1) to (10.3) exhibit the above pattern all the year round, but the magnitude of fluctuations decreases with increasing depth. This is due to the longer pathways that incoming water flux has to travel, eventually mixing with greater volumes of water already present in the aquifer.

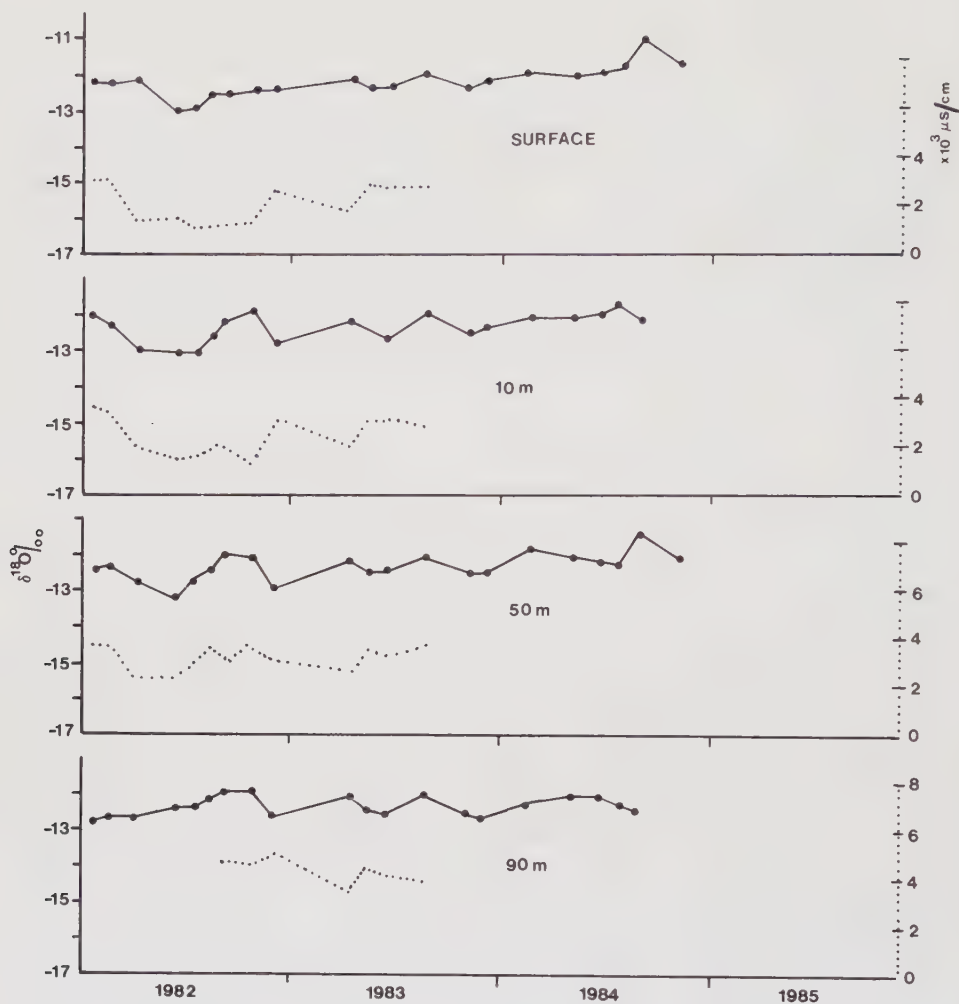


Fig.(10.4) $\delta^{18}O$ (full line), water table (dashed line) and electrical conductivity (dotted line) of groundwater in borehole G9, Finnsjön.

For the sake of illustration, temperatures recorded at the sampling depths of one of the boreholes, G5, are shown in Fig.(10.5). It is seen that in all the boreholes groundwater is generally above the 4°C isotherm at 10 m depth. Thus, the possibility that water at 4°C can sink to deeper depths and bring about a quick longitudinal mixing is little. Temperature gradients below 10 m depth are also very small. These small gradients cannot generate the large-scale convective mixing, necessary to change the δ values of the groundwater by about 2‰, as is observed after the 1982 snowmelt.

The behaviour of G9, Fig.(10.4) was quite different than boreholes G3 to G7. It showed little or no decrease in its $\delta^{18}\text{O}$ in April 1982 and 1983, and exhibited almost constant value all the year round. Topographically G9 lies in the discharge zone, implying that water fluxes reaching it get well mixed because of longer flow paths and greater residence time. This is further supported by the electrical conductivity measurements. G9 has a higher electrical conductivity ranging from 1500 to 6000 $\mu\text{S}/\text{cm}$, while G3, G5 and G7 representing the recharge zone have the corresponding values between 150-400 $\mu\text{S}/\text{cm}$.

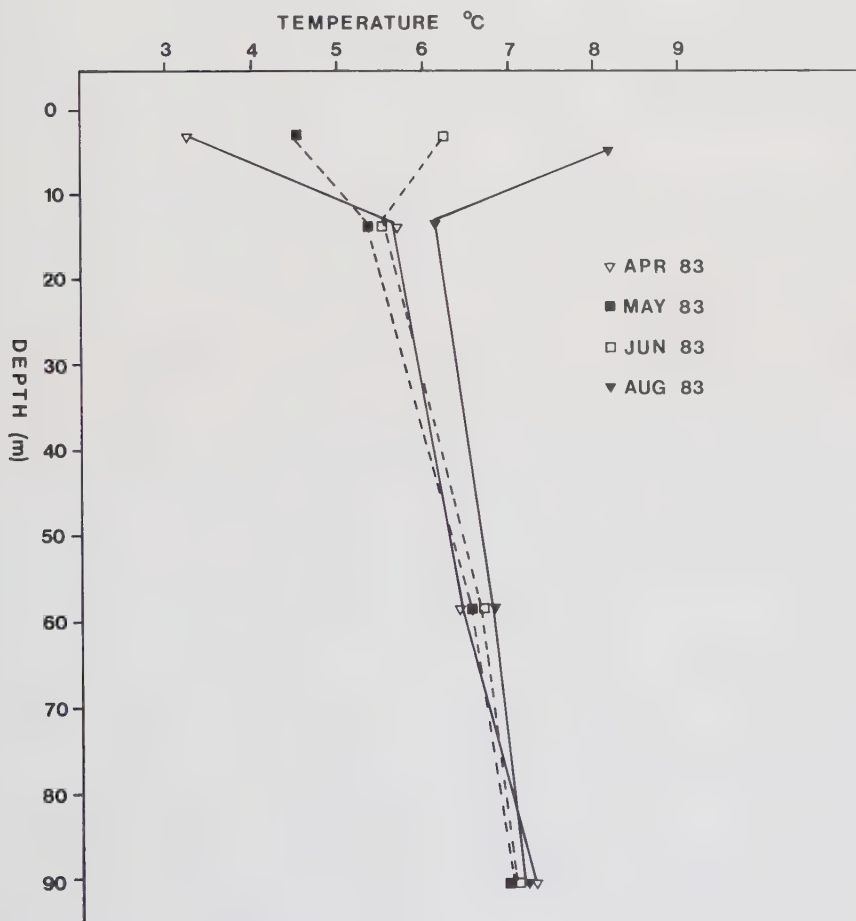


Fig.(10.5) Temperature profile of groundwater in borehole G5, Finnsjön.

10.7 Conclusions

^{18}O can be employed to study surface and groundwater interactions in fissured rocks. It may be possible to determine the transit time of infiltrating surface inputs in the shallow part of the aquifer if an intensive sampling schedule is maintained. The identification of local recharge-discharge zones is quite amenable to the ^{18}O method. For studies on groundwater acidification, the isotope method may prove its utility in demarcating the recharge-discharge zones.

11 CONCLUDING REMARKS

Theoretically, the basic principles of isotopic fractionation during evaporation-condensation and molecular exchange with the atmosphere for an open water mass are quite well known. So long as the weather conditions, i.e., temperature, relative humidity and potential evapotranspiration etc., remain constant, the observed and predicted δ values of a water body are in close agreement. Generally, in nature, the weather conditions vary almost daily and a compromise has to be made by using average values of temperature, relative humidity and potential evapotranspiration, etc., introducing errors in the estimation of $\delta_{\text{evaporate}}$, i.e. δ_E .

For water balance studies using environmental isotopes (^{18}O or D), the main problem is an accurate estimation of δ_E . A direct experimental method to measure δ_E has yet to be found.

The pan evaporation experiments show that in humid climates, such as central Sweden, the magnitude of error in the estimates of δ_E is small and that ^{18}O can be employed for lake water balance studies. Similarly, in stream runoff and regional water balance studies, corrections can be made for the isotopic fractionation due to direct evaporation from the sheet flow before water inputs infiltrate in the soil or mix with stream water. The necessity of such corrections is dictated by the forested area, the overall climatic (semi-arid or humid, etc.) conditions and the general topography of the basin.

The weighted monthly mean $\delta_{\text{precipitation}}$ and monthly mean surface air temperatures are well correlated and so is the case for δ_{vapour} and specific vapour density. Even δ_{vapour} and monthly mean surface temperature show a high correlation. Further, precipitation and atmospheric vapour are in near isotopic equilibrium during the summer months. In terms of the isotopic data, Uppsala can be treated as an inland station, though it is quite close to the east coast. On a global scale, only inland stations show high correlations between $\delta_{\text{precipitation}}$, δ_{vapour} and temperature.

Thus from the interrelationships among $\delta_{\text{precipitation}}$, δ_{vapour} and mean surface air temperature (all on a monthly basis), a reasonable guess of $\delta_{\text{evaporate}}$ can be made for regions where data

either on surface temperatures or $\delta_{\text{precipitation}}$ are available, which has a direct bearing on the water balance studies. The temperature lapse rate of $\delta_{\text{precipitation}}$ and the slope of δ_{vapour} versus specific vapour density (natural log) indicate that the transport of atmospheric moisture from the trade-wind belts to the poles is predominantly eddy in nature.

When the "rest time" of rain water in the rain gauges is known, it is possible to apply corrections for ^{18}O fractionation in the rain gauges in remote areas where weekly or twice as frequent sampling schedule is maintained. The rest time can be obtained from the precipitation collection network.

Preliminary studies on the fractionation of throughfall in a pine forest show that, in general, the throughfall is slightly enriched with respect to the rainfall. The enrichment or depletion in throughfall can be qualitatively predicted from a standard curve drawn between $(\delta_{\text{ss}} - \delta_{\text{a}})$ and the relative humidity; δ_{ss} is the δ value of the canopy reservoir at the isotopic steady state and δ_{a} is the δ value of the atmosphere. Also, the simulated $\delta_{\text{throughfall}}$ values (using a canopy fractionation model) agree closely with those observed. This implies that if the relative humidity at the tree canopy level is recorded during a storm, a fairly accurate estimation of $\delta_{\text{throughfall}}$ is possible provided the rain is uniform in its isotopic distribution relative to time. In general, when the tree canopy area is considerable, the amount and δ value of net rainfall eventually reaching the soil surface will be different than the observed values from the rain gauges. The above has greater impact on water balance studies in the semi-arids. On the other hand, the isotopic enrichment of throughfall is small in humid climates, yet the interception loss by the tree canopy is of consequence to almost all climatic settings.

The present study gives a good example of the utility of ^{18}O as a natural tracer of soil moisture movement. The seasonal percolation and in some cases the eventual groundwater recharge have been determined. Specially, the ^{18}O -depleted snowmelt water that infiltrates the soil tags the soil moisture with low $\delta^{18}\text{O}$ values. Sometimes, even the relatively enriched moisture contributed by the summer rains can be used as an environmental tracer of soil moisture. The downward movement of the depleted or enriched soil moisture gives an accurate and direct measure of the rate of soil moisture movement, i.e. the water particle velocity and the moisture flux through a certain level in the unsaturated zone. The main advantage of the ^{18}O method is that from only one

profile of soil moisture and its ^{18}O distribution, the annual percolation between two consecutive melt periods or summers can be determined, provided the depleted or the enriched moisture layers representing the two events, separated a year apart, can be identified in the soil. Experiments show that the method is very effective in homogeneous soils and the residence time of infiltrating moisture in the different soil zones can be estimated also. This has a direct bearing on monitoring the movement of nutrients and pollutants in the unsaturated zone. The ^{18}O method is completely free from radiation hazards, has no effect on the ecology of the environment and the problem of estimating retardation due to adsorption in the soil does not arise.

Lysimeter studies show that in the glacio-fluvial and till deposits (central Sweden), the isotopic fractionation in the unsaturated zone is expected to be less than 1‰ during the summer season.

Oxygen-18 as a tracer has also been found to be amenable to studies on surface and groundwater interactions (mixing) and identification of local recharge-discharge zones. The seasonal ^{18}O fluctuations of surface water inputs from snowmelt and summer rains have been found to be reflected in the groundwater (5 to 90 m depth) in fissured rocks at Finnsjön. The quick decrease and then increase of the $\delta^{18}\text{O}$ of groundwater after snowmelt and summer rains indicates fast infiltration of water through the fissures in the rock in the recharge zone. Conductivity measurements of the groundwater and water table fluctuations also support the inferences drawn from ^{18}O tracing.

It is concluded that armed with a clear knowledge of the fundamental processes of isotopic fractionation in nature, important field hydrological problems, e.g., groundwater recharge-percolation, soil moisture movement, surface and groundwater interactions, and water balance, can be successfully studied in a completely different physical perspective.

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LIST OF SYMBOLS

A	Area	cm ²
Å	Ångström	10 ⁻⁸ cm
Bq	Becquerel	disintegrations per second
C	Free throughfall coefficient.	
d	Depth of water	cm
E	Evaporation	mm/d
	also: Net flux of H ₂ ¹⁶ O from liquid to gaseous phase.	
E*	Net flux of H ₂ ¹⁸ O from liquid to gaseous phase.	
F _{gl} , F* _{gl}	Fluxes of H ₂ ¹⁶ O and H ₂ ¹⁸ O molecules from the gaseous to the liquid phase respectively.	
F _{lg} , F* _{lg}	Fluxes of H ₂ ¹⁶ O and H ₂ ¹⁸ O molecules from the liquid to the gaseous phase respectively.	
F _{ll} , F* _{ll}	Fluxes of H ₂ ¹⁶ O and H ₂ ¹⁸ O molecules to the pan or water mass or liquid phase respectively.	
f	Ratio of volume at any instant to original volume of water.	
h	Relative humidity.	
I	Inflow.	
K	Thermodynamic equilibrium constant.	
K'	Constant.	
K _{gl} , K* _{gl}	Resistances of the interface to H ₂ ¹⁶ O and H ₂ ¹⁸ O molecules from the gaseous (vapour) to the liquid (water) phase respectively. Henceforth written as gaseous and liquid phases only.	
K _{lg} , K* _{lg}	Resistances of the interface to H ₂ ¹⁶ O and H ₂ ¹⁸ O molecules from the liquid to the gaseous phase respectively.	
L	Unit of length	mm or cm
M	Amount of water vapour (section 3)	g
	also: Saturation mixing ratio and time averaged humidity of air (section 5).	
m	Amount of moisture passing through a certain level in the soil.	

N_0	Total number of molecules in the liquid phase (initially).	
N_g, N_g^*	Number of $H_2^{16}O$ and $H_2^{18}O$ molecules in the gaseous phase (atmosphere) respectively.	
N_l, N_l^*	Number of $H_2^{16}O$ and $H_2^{18}O$ molecules in the water or liquid phase respectively.	
O, O^*	Oxygen atoms $^{16}O_8$ and $^{18}O_8$ respectively.	
P_i	Precipitation in month i since 1952	mm
Q	Outflow.	
q	Specific vapour density (section 5)	g/m^3
also:	Average moisture flux (section 8)	mm/d
R	Gas constant (section 3)	J/K/mol
also:	Ratio of $H_2^{18}O$ to $H_2^{16}O$ molecules in a given phase (section 3)	
	Amount of rain (section 7)	mm
	Groundwater recharge (section 8)	mm
R_0	Critical amount of rain necessary to saturate the canopy reservoir	mm
$R_g, R_l, R_{ll}, R_{STD}$, etc.:	Ratios of $H_2^{18}O$ to $H_2^{16}O$ molecules in the gaseous and liquid phases, inflow to a pan, and standard water respectively.	
r_{gl}	Ratio of the resistances of the interface to the flux of $H_2^{18}O$ and $H_2^{16}O$ molecules from the gaseous to the liquid phase respectively.	
r_{lg}	Ratio of the resistances of the interface to the flux of $H_2^{18}O$ and $H_2^{16}O$ molecules from the liquid to the gaseous phase respectively.	
S	Amount of water in a pan or a water mass (section 3)	
also:	The canopy reservoir or saturation capacity (section 7)	mm
SMOW	Standard Mean Ocean Water	
T	Temperature, generally given in $^{\circ}C$, but sometimes in Kelvin as specified in text.	
T	Throughfall (section 3)	mm
T_i	Tritium concentration in precipitation in month i	Bq or TU
T_p	Total tritium input since 1952 corrected for decay	Bq or TU
T_s	Total amount of tritium in the soil to a certain depth	Bq or TU
TU	Tritium units	7.2 dpm/l water
t	Time (section 7 & 8)	

V	Volume	cm ³
VSMOW	Vienna(SMOW)	
v	Velocity	mm/d
z	Depth	cm
α	Unit separation or fractionation factor	
β	Reciprocal of the ratio of the resistances of the interface to the flux of H ₂ ¹⁸ O to H ₂ ¹⁶ O molecules from the gaseous to the liquid phase.	
δ	The relative difference in the ratio of H ₂ ¹⁸ O to H ₂ ¹⁶ O molecules of the sample with respect to a standard	‰
Δc	Equivalent to an excess separation factor.	
Δt	A small interval of time.	
θ	Average soil moisture (vol%).	
θ_j	Average soil moisture (vol%) of a soil section j.	
μS	Micro Siemens	
δ_a, δ_g	δ values of air, atmospheric moisture or gaseous phase respectively	‰
$\delta_E, \delta_I, \delta_l, \delta_p, \delta_Q$	δ values of the evaporate, inflow a water mass, precipitation and outflow respectively	‰

If any of these symbols stands for another quantity or unit, it is specified within the text at the appropriate place.

